A hydrological and nutrient load balance for the Lake Clearwater catchment, Canterbury, New Zealand

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by

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Abstract

The Lake Clearwater catchment, in the Canterbury high country of New Zealand, has a native ecosystem that is adapted to low nutrient conditions. Wetlands in the catchment are identified by the Department of Conservation's Arawai Kākāriki Wetland Restoration Programme as one of three important endemic wetland types in New Zealand. Uncertainty regarding diffuse nutrient load from agriculture into the lake and wetland ecosystems is limiting effective management of the catchment. This study investigated hydrological processes and nitrogen and phosphorus concentrations to improve knowledge of the sources, characteristics and magnitude of nutrient loading from agricultural land use in this 46 km^2 high country catchment.

Relevant hydrological data and literature pertaining to the catchment was extensively reviewed. In addition, flow for five key surface waterways was continuously logged at ten sites for 2 years. Concurrently, nutrient concentrations for total nitrogen, nitrate, ammoniacal nitrogen, total phosphorus and dissolved reactive phosphorus were measured at ten surface water sites and three groundwater sites. Total nitrogen and phosphorus load from farmland was calculated from annual flow and median concentrations for four waterways: farmland perennial stream runoff, farmland ephemeral stream runoff, a wetland channel below the farmed hillslope and the lake outlet. Similarly, total nitrogen and phosphorus load for unfarmed land was calculated from the flow and median concentration of two un-impacted perennial streams. Total nitrogen and phosphorus mass balances were calculated and used to estimate subsurface nutrient load and runoff volume from the farmed hillslope. Estimates of subsurface runoff were also made using Darcy's equation and a water balance. Nutrient load predictions from the Catchment Land Use for Environmental Sustainability (CLUES) model were compared to measured loads.

Nutrients were found to be elevated downstream of farmland, especially nitrogen, which was often above relevant guidelines and typical concentrations in upland waterways in Canterbury. Nitrate in farmland subsurface runoff was elevated and was estimated to contribute 52% of total nitrogen yield from farmland. Total nitrogen yield (1.96-2.94 kg ha^{-1} $year^{-1}$) for farmed land was comparable to minimum values for pastoral land use in literature but total phosphorus yield (0.093-0.123 kg ha^{-1} $year^{-1}$) was well below published values. The range in yield estimates is due to subtraction of a high and a low estimate of natural baseline yield from the measured in-stream yield.

Total nitrogen export from the lake (2518 kg $year^{-1}$) was greater than estimated input (1375 kg $year^{-1}$) from farmed and non-farmed land indicating an additional source of nitrogen into Lake Clearwater. Total phosphorus export from Lake Clearwater of 58 kg $year^{-1}$ was 24% less than total estimated loads into the lake (76 kg year-1) from farmed and non-farmed land. Phosphorus was not often above relevant guidelines and the median total nitrogen to total phosphorus ratio in Lake Clearwater (49:1) indicated phosphorus is the limiting nutrient in the lake. Because phosphorus was less elevated relative to nitrogen, an increase in phosphorus inputs could have a greater effect on productivity in the wetland and lake. With corrected land use information, total nitrogen loads predicted by the CLUES model were reasonable but total phosphorus loads were greatly overestimated. Investigation into potential impacts of the elevated nutrient loads described in this study on receiving native ecosystems is recommended to inform conservation efforts.

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Conference presentations

Wadworth-Watts H.D., Caruso B.S., O'Sullivan A.D., and Clucas R. (2012) *Sources of Nutrient Loading in the Lake Clearwater Catchment, Canterbury, New Zealand.* New Zealand Hydrological Society Conference, 27-30 November 2012, Nelson, New Zealand

Wadworth-Watts H.D., Caruso B.S., O'Sullivan A.D., and Clucas R. *(2011) Hydrological and Nutrient Transport Balances for an Intermontane Catchment, Canterbury, New Zealand.* New Zealand Hydrological Society Conference, 5-9 December 2011, Wellington, New Zealand.

1 Introduction

Native intermontane tussock wetlands in the Lake Clearwater catchment and Hakatere area are identified as an important endemic wetland type in New Zealand (Department of Conservation 2008; Myers et al. 2013). A goal of the Arawai Kākāriki Wetland Restoration programme is to “undertake research to improve understanding of wetland restoration issues and to develop best practice wetland management and monitoring tools” (Department of Conservation 2008). The research in this thesis contributes towards reaching that goal. Environment Canterbury (ECan) also recognises the indigenous biodiversity, community and water quality values of these natural wetlands. The Proposed Canterbury Land and Water Regional Plan (Environment Canterbury 2012) states that land use must be carefully managed to avoid nutrient enrichment in high country streams and wetlands that are adapted to low nutrient conditions. The plan introduces requirements for agricultural land use in sensitive lake and wetland catchments. Requirements include deriving annual nutrient budgets to estimate nitrogen losses and formal farm environmental plans to ensure best practice.

While water quality in Canterbury’s high country waterways is generally good, land use intensification is having “noticeable deleterious effects” in some areas (Stevenson et al. 2010). Investigation of water quality at smaller spatial (catchment) is needed to complement regional scale monitoring in Canterbury and New Zealand (Stevenson et al. 2010). From a biogeochemical and hydrological perspective, the most appropriate scale to delineate an ecosystem is the catchment scale, which includes interconnected terrestrial, groundwater and surface water habitats (Schallenberg et al. 2011). Non–point source pollution from agriculture is a problem worldwide and in New Zealand. Non-point source pollution in this study is defined as elevated diffuse nutrient loss from agricultural land into waterways. A review of nutrient cycling processes and sources, effects of elevated nutrient concentrations and water quality benchmarks relevant to this study is included to place this study in context. Studies of diffuse agricultural pollution in New Zealand and internationally typically focus on lowland farming areas. However, the Lake Clearwater valley is a semi pristine inter-montane environment that does not resemble lowland farming areas. The Catchment and Land Use for Environmental Sustainability (CLUES) model (Semadeni-Davis et al. 2011) has been developed in New Zealand to predict Total Nitrogen (TN) and Total Phosphorus (TP) load into waterways from agricultural land use. Results from this study will be compared to predictions of TN and TP loads made by the CLUES model (section 1.5) to assess the model’s reliability in high country catchments.

Little is known about the susceptibility of the Lake Clearwater wetlands and high country waterways to elevated nutrient loading. In addition, little is known about the magnitude and type of nutrient loads that the wetlands within the Lake Clearwater catchment are receiving. This study aims to improve knowledge of the sources, characteristics and magnitude of nutrient loading to high country wetlands in Canterbury to provide information for relating changes in wetland ecosystems to potential nutrient loading.

1.1 Research objectives

The focal point of this research project was the hypothesis that the extent of diffuse nutrient pollution from farming activities in the Lake Clearwater basin is sufficient to have an adverse effect on water quality, and hence ecosystem integrity, in the Lake Clearwater Catchment. The objectives of this Master's thesis are to:

1) Investigate the hydrology and water quality of the Clearwater catchment by:
    a. Reviewing meteorological, climate and existing flow data relevant to the area to obtain key water balance parameters: these include precipitation, evapotranspiration, groundwater runoff and surface water runoff.
    b. Monitoring surface water flows at key locations in the catchment over a significant period of 48 months from 2010 to 2012, thus improving water balance parameters and nutrient loading calculations by providing more accurate stream flow data.
    c. Performing a water balance of the Lake Clearwater Catchment on an annual scale to estimate unmeasured surface water and groundwater runoff contributions to nutrient loading.

1) Investigate the water quality of the Clearwater catchment by:
    a. Sampling surface water quality at nine locations during a range of flow events to estimate nutrient concentration in important surface waterways.
    b. Sampling groundwater quality at three locations down-slope of the farmed area to estimate nutrient concentration in subsurface runoff from farmland.
    c. Performing a nutrient mass balance over the Lake Clearwater catchment to quantify sources, loading, and transport pathways of nutrients.

2) Assess the CLUES model's applicability to a New Zealand high-country catchment and improve CLUES model predictions of nutrient loadings in the Lake Clearwater catchment.

1.2 Nutrient cycles

Nitrogen is highly reactive; it is subject to biogeochemical processing and transformation in soil and waterways. Metabolically active redox gradients in streambed hyporheic zones facilitate nitrogen transformation, uptake and denitrification (Alexander et al. 2007). Nitrogen transformations are primarily microbially catalysed redox reactions (Figure 1-1). The incorporation of NH_4^+ into organic matter (amination) or its release (deamination or ammonification) is the only non-redox reaction involving a nitrogen transformation in the nitrogen cycle.

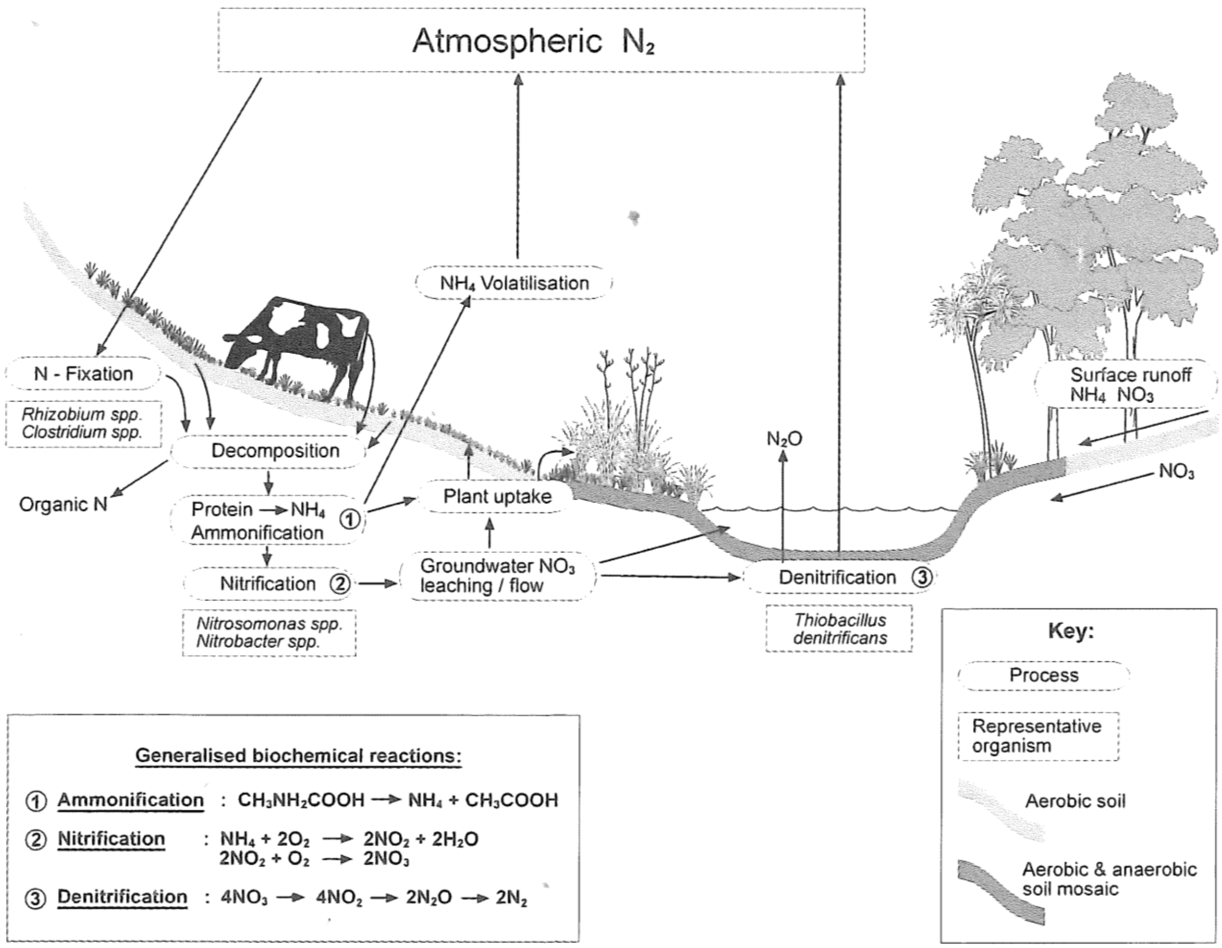

Figure 1-1, Generalised nitrogen cycle for a farmed hillslope in New Zealand (Harding et al. 2004)

Rural nitrogen inputs to soil typically include nitrogen fertilizer, animal faces and urine, nitrogen fixation and atmospheric deposition. The distribution of these inputs and the environmental setting, e.g. climate, topography, vegetation and soil properties, affects how nitrogen is transported from land to water. The environmental setting also dictates the agricultural land use (types of nitrogen sources) (Alexander et al. 2007).

Nitrate in runoff is often produced on farmland when nitrification of ammonium results in more nitrate than microbes and plants in the soil can use. This excess of ammonium is most commonly due to concentrated animal urine, faeces and/or fertilizer (Burt et al. 1993). Nitrate is considered a "bioavailable" form of nitrogen(Burt et al. 1993), and therefore is likely to contribute to potential eutrophication of the wetland and Lake Clearwater if its concentration is elevated. Nitrate is highly soluble and is transported easily in surface water and groundwater (Harding et al. 2004). Leaching and subsurface flow of nitrate is an important pathway for nitrogen loss from farmland in Canterbury (Environment Canterbury 2012) and the most important effect on groundwater from agriculture in New Zealand (Murray and Ackroyd 1979). Bayer et al (2008) found 30% of nitrogen entering Lake Hayes, an intermontane eutrophic lake in Otago, was from nitrate in groundwater.

Nutrients from faeces, urine and fertilizer can be rapidly transported by overland flow into surface water (Harding et al. 2004), when this happens there is little opportunity for pasture to utilize nutrients. In many areas of New Zealand where soils are permeable, the majority of saturated overland flow occurs in 'critical source areas' where soils are saturated much of the time (Monaghan et al. 2007). In addition to saturated subsurface flow, reduced permeability can cause overland flow. Soil compaction from cultivation or treading damage can cause reduced permeability (Elliott and Sorrell 2002). Direct input into surface waterways of fertilizer or animal faces and urine is also an important nutrient loss mechanism from farmland.

However, overland flow may not be the only important mechanism for nutrient runoff losses, especially in low rainfall areas with free draining soils. In Western Australia, Ocampo et al (2003) reported elevated nitrate runoff during sharp increases in ground saturation. Results showed that pre-event or "old" water dominates (>70 %) in flow responses to rain events and elevated nitrate concentrations were seen in shallow near-stream bores and stream flow at the point when connectivity was observed between a upland aquifer and near-stream zones. Ocampo et al (2003) concluded that upland or non-riparian catchment land could act as perched aquifer storage for water and nitrates until a point when groundwater levels are sufficient to permit a connection between the upland storage of old water and the near stream areas that are directly contributing to stream flow. The study catchment in Ocampo et al. (2003) receives 850 mm of annual rainfall and has primarily ephemeral stream flow.

Figure 1-2 show a typical phosphorus cycle for a farmed hillslope. Plants take up dissolved reactive ionic forms of phosphorus such as orthophosphate (PO_4^{+3}). Phosphorus is released back to soil from decomposing organic matter, urine and faeces. Phosphorus in fertilizer is also a common source of phosphorus on farmland (Harding et al. 2004).

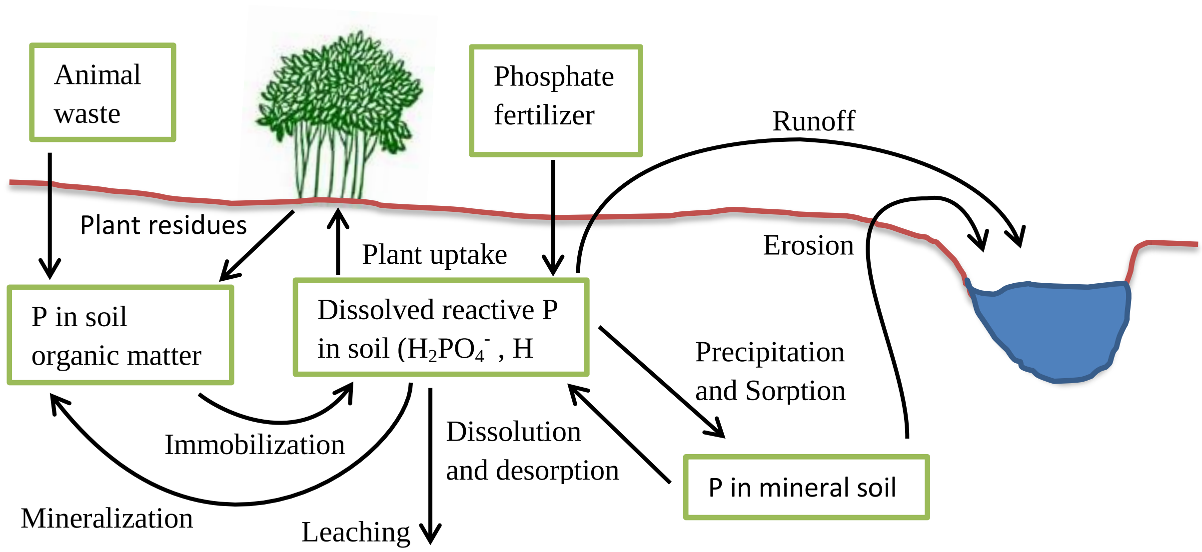

Figure 1-2, The phosphorus cycle

Phosphorus tends to be carried to streams, bound to sediment, via overland flow. Erosion can greatly increase losses of phosphorus from farmland (Elliott and Sorrell 2002; Harding et al. 2004) and TP has been shown to increase during storm events in New Zealand (Caruso 2000; Elliott et al. 2005). Phosphorus can also be elevated in the early stages of a high flow event (McDiffett et al. 1989) as accumulated phosphorus is flushed from near stream sources. Direct input of urine and faeces is also a common source of phosphorus that is not subject to any attenuation (Harding et al. 2004). Once in streams total phosphorus (TP) is typically attenuated more rapidly than total nitrogen (TN) (Alexander et al. 2002). Phosphorus is also commonly attenuated in lakes (Kõiv et al. 2011).

Surface and subsurface nutrient loss pathways delay transport of nutrients from land sources to waterways (Alexander et al. 2007; Elliott and Sorrell 2002). Therefore, short term measured loads may not represent eventual loads for a land use. Similarly, due to long residence times, lake water quality may be indicative of nutrient loads that occurred at some time in the past rather than loads from current land use. To determine catchment export coefficients and loads, at least five years of monitoring is desirable to smooth out inter-annual variability account for transport delays. Modelling of expected changes from current catchment conditions is often needed for effective management (Elliott and Sorrell 2002).

1.3 Effects of nutrient loading

In the Lake Clearwater catchment the primary concern is the contribution of nutrients from diffuse sources arising from pastoral agriculture, and the potential for increased loads as land use becomes more intensive (Robertson and Suggate 2011). Nitrogen and phosphorus yield from agricultural pastoral land use is much higher than yield from unfarmed land (Cooper and Thomsen 1988; Quinn and Stroud 2002) and wetlands in New Zealand are increasingly under threat from agricultural land use (Myers et al. 2013). Nitrogen and phosphorus are needed for vegetative growth, the base of any ecosystem. However, nutrients can act as pollutants. The aquatic ecosystems in the Lake Clearwater catchment and many upland catchments have naturally evolved with low nutrient conditions. If nutrients are too abundant they can cause negative environmental effects such as eutrophication, invasive vegetative growth and loss of native habitats (Elliott and Sorrell 2002). The growth of photosynthetic aquatic organisms is often controlled by the concentrations of dissolved inorganic nitrogen (NH_4^+, NO_3^-) and phosphorus (PO_4^{3-}) (Harding et al. 2004). Elevated nutrient concentrations could cause invasive aquatic and terrestrial species to displace native species in wetlands and lakes in the Hakatere area (Figure 1-4)(Myers et al. 2013).

Schallenberg and Sorrell (2009) found that lakes in New Zealand changing from a clear-water to a turbid state is positively correlated with the percentage of the lake catchment in pasture. Higher nutrient loading can also favour phytoplankton and epiphyton growth over macrophytes, further diminishing water clarity. The clear water of Lake Clearwater may be dependent on the ability of macrophyte cover on the lakebed to limit sediment resuspension from wind-induced turbulence. In turn, macrophytes are dependent on clear water to allow sufficient light penetration for photosynthesis. Lake Clearwater has become less clear between 2004 and 2012 and macrophyte bed cover is showing signs of reducing (Adrian Meredith personnel communication 2012). According to the lake trophic level index monitoring, which includes the proportion of macrophyte bed cover, Lake Clearwater changed from oligotrophic in 2005 to mesotrophic in 2007 (Enviroment Canterbury, 2008). TN in the nearby Lake Camp increased from 0.2 g m^{-3} to 0.33 g m^{-3} in this period (De Winton 2008). Other lakes in the Hakatere area (Figure 1-4) also increased in TN in this period. Phytoplankton and epiphyton growth in many lakes in the northern hemisphere is typically phosphorus limited. However, Lakes in New Zealand are sometimes nitrogen limited (Harding et al. 2004). Abell et al. (2010) suggested that TN:TP (by mass) "greater than 15:1 is indicative of potential P-limitation, TN:TP less than 15:1 and greater than 7:1 is indicative of potential N- and P co-limitation, and TN:TP less than 7:1 is indicative of potential N-limitation". If the limiting nutrient increases, the phytoplankton may increase, leading to less clear water and decreasing macrophyte bed cover.

Although much progress has been made in recent decades around pollution control in waterways, wetlands are very sensitive to the amount of nutrients they receive, and many New Zealand wetlands continue to suffer excess nutrient inputs (Myers et al. 2013). Nutrient loading into waterways resulting from agriculture in lowland areas is a major problem in New Zealand and worldwide and is well documented for lowland farming (Burt et al. 1993; Harding et al. 2004; Myers et al. 2013). Fewer studies focus on upland areas and little is known about nutrient pollution in high country areas such as tussock grasslands or wetlands (Caruso et al. 2010; Robertson and Suggate 2011). As agricultural land-use in high country areas becomes more intensive the potential for elevated nutrient loadings into previously low-nutrient waterways increases. The quantity of nutrients in streams and wetlands in the Hakatere area is of concern because invasive plant species have the potential to degrade the especially sensitive native ecology of the wetland systems and reduce biodiversity (R. Clucas, personnel communication, 2011).

1.4 Water quality benchmarks in New Zealand

Water quality standards for nutrients are not well developed in New Zealand (Land & Water Forum 2010). The most common guidelines used as a benchmark for water quality in New Zealand are the Australian and New Zealand Environment and Conservation Council guidelines (ANZECC 2000). These guidelines provide “trigger values” for various water quality indicators for lowland and upland rivers in New Zealand and Australia. Trigger values provide a median concentration of certain toxicants that should not be exceeded to avoid significant impact on in-stream aquatic biota. For instance, a default trigger value of a specific concentration is provided at the 99% species protection level for New Zealand upland rivers. This indicates that at this concentration 99% of aquatic biota will not be negatively impacted. The ANZECC guidelines are intended to be conservative to trigger a management response before significant impacts occur. In the absence of guidelines more specific to the waterways found in the Lake Clearwater, the ANZECC guidelines are a useful measure of water quality. ANZECC guideline trigger values for upland rivers are used in this study. The New Zealand Ministry for the Environment also provides values that should not be exceeded to avoid excessive growth of periphyton (Ministry For the Environment 1992). The ANZECC and MfE guidelines are shown in Table 1-1.

Table 1-1, ANZECC trigger values and MfE guidelines in New Zealand for slightly disturbed upland river ecosystems

	TN	**NO_3**	**NH_4^-**	**TP**	**DRP**	**DO**	**pH**
ANZECC	0.295 g m^{-3}	0.167 g m^{-3}	0.01 g m^{-3}	0.026 g m^{-3}	0.009 g m^{-3}	99-103% Saturation	7.3-8 S.U.
MfE		0.04-0.1 g m^{-3}			0.015-0.030 g m^{-3}		

Another measure of water quality in the Lake Clearwater catchment is comparison of measured water quality parameters with similar waterways in Canterbury, waterways with catchments both impacted and un-impacted by agricultural land use. Comparison with regional scale monitoring can be used to ascertain if concentrations of nutrients in a waterway are natural or the result of a land use impact. Stevenson et al. (2010) state that many rivers and streams in Canterbury face issues with nutrient enrichment due to intensification of land use; careful management is recommended in upland areas to safeguard the current water quality. Smaller scale studies, such as this one, will also help give a more complete picture of Canterbury water quality.

1.5 Background to the CLUES model

The Catchment Land Use for Environmental Sustainability model (CLUES) (Semadeni-Davis et al. 2011) has been developed in New Zealand to predict changes in water quality and nutrient loads due to changes in land use. CLUES is primarily intended for large catchments or regional-level studies. The model was developed and calibrated largely with lowland data and to date has not been assessed for its performance in high country catchments.

CLUES currently estimates loads, yields and concentrations for TN, TP, sediment and *E. Coli*. CLUES also provides an estimate of economic output for a given land use. The model runs within a GIS platform (ArcMap) and inputs are contained in spatially explicit data layers. Further information can be found in Semadeni-Davis et al. (2011).

The CLUES model framework contains a sub model, SPARROW (SPAtially-Referenced Regression On Watershed attributes). SPARROW predicts the nutrient load, yield and concentration results of CLUES for non-pastoral land use in each catchment. This model was originally developed by the United States Geological Survey (USGS) (Schwarz et al. 2006) to relate water quality measurements to catchment land use and other attributes. The core component of the SPARROW model contains nonlinear regression equations that attempt to describe non-conservative transport of contaminants from point and diffuse sources to rivers and through a spatially explicit river network. For each sub-catchment, the nutrient load generated from diffuse sources is calculated primarily from the area of each land use (ha) multiplied by a source coefficient (kg/ha/yr). Sukias et al. (2005) Alexander et al. (2002) and Schwarz et al. (2006) describe model calculations in more detail. SPARROW was first applied in New Zealand by Alexander et al. (2002) for the Waikato River catchment. Model parameters for SPARROW in New Zealand were then calibrated to measured loads in the entire New Zealand national water quality network (Elliott et al. 2005). Measured loads from high country farming, like that in Lake Clearwater catchment, are not represented in the calibration dataset for the current SPARROW parameters. In addition, the monitoring network does not include measurements from catchments less than 10 km^2, the smallest being 13.7 km^2. Elliott et al. (2005) state that CLUES loads from catchments smaller than 10 km^2 should be used with caution. OVERSEERER (AgResearch 2013), a farm scale nutrient budget model, is used in CLUES to produce estimates of nutrient loss to waterways for agricultural land use. Like SPARROW, OVERSEER is developed to predict loads in common lowland farming scenarios.

Due to the lack of measured loads from catchments and land use similar to that found in the Lake Clearwater catchment in the calibration data set, prediction of loads in Lake Clearwater catchment is outside the typical scope of the model. Results of this study will indicate the reliability of CLUES predictions in high country catchments. In addition, results from a comparison of predictions and measured values may be able to be incorporated into future versions of the model to improve predictions for catchments of this type.

1.6 Study Location

The Lake Clearwater catchment is located in the Hakatere (Ashburton Lakes) area (Figure 1-4) inland from the township of Mt Somers, Canterbury, New Zealand. The Catchment is located on the eastern side of New Zealand's Southern Alps (Figure 1-3).

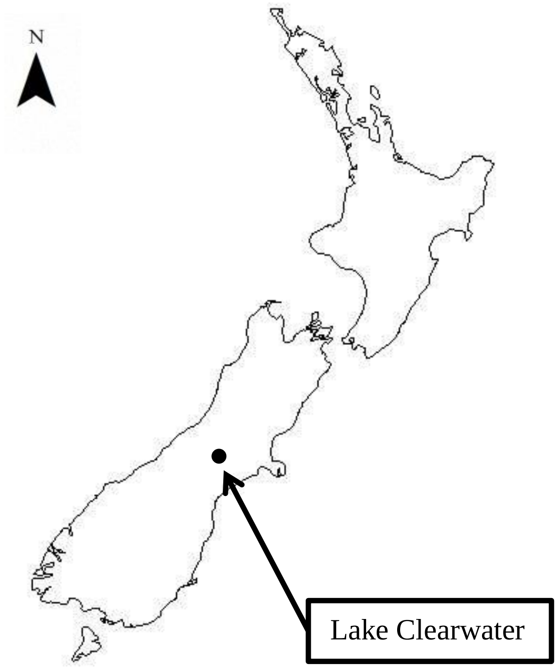

Figure 1-3, Location of Lake Clearwater, New Zealand

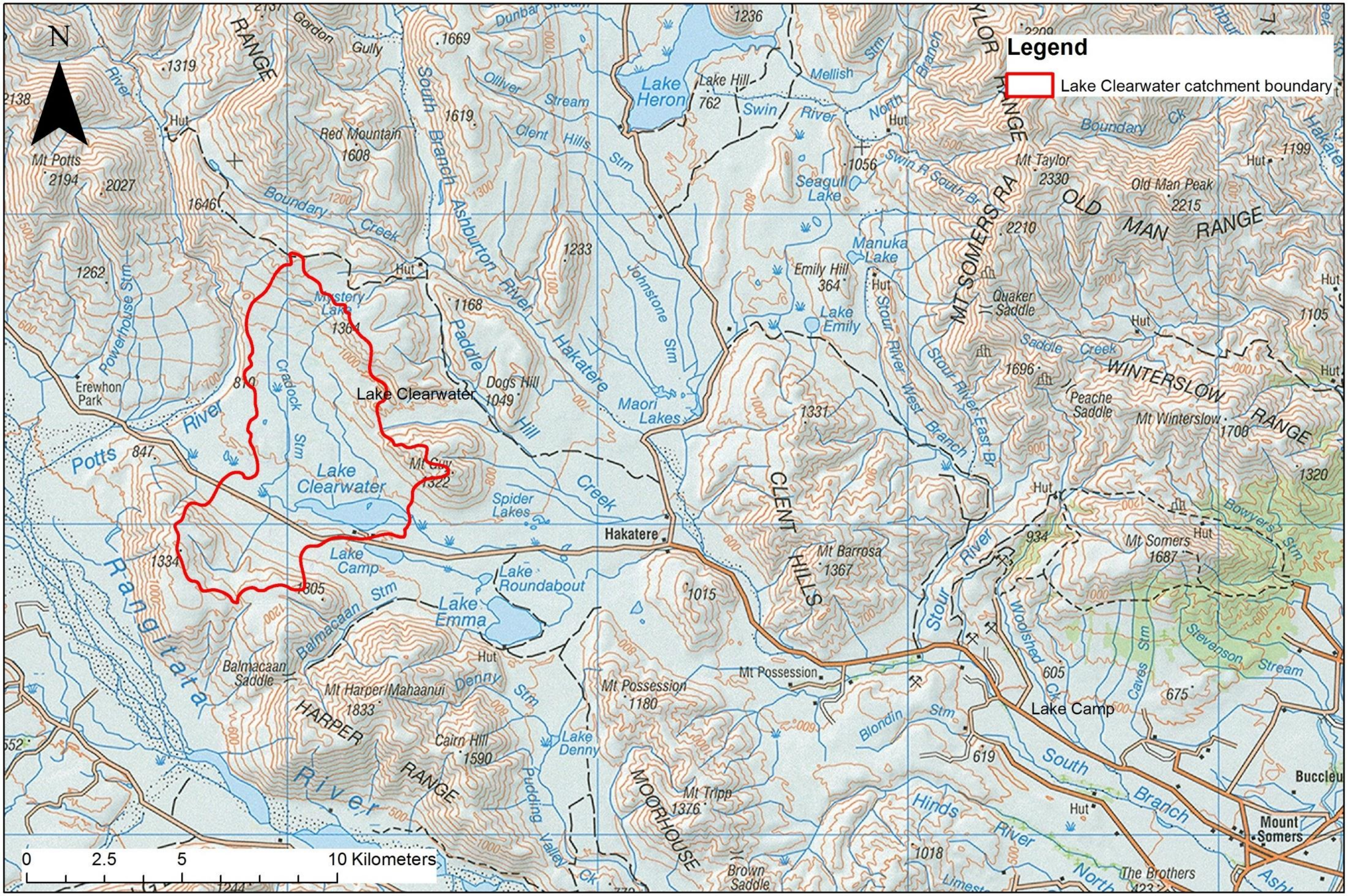

Figure 1-4; Map showing the Lake Clearwater Catchment in the Hakatere area (Land Information New Zealand, 2009)

1.6.1 Study area topography

The focus of this study is the 46 km^2 Lake Clearwater Catchment contained within the Hakatere area (Ashburton Lakes District). The Hakatere area is an intermontane basin on the eastern side of the Southern Alps inland from the township of Mt Somers. The Lake Clearwater catchment is in an elevated valley, cut off from the much larger Rangitata River valley, within the Hakatere basin. The valley floor and wetland area is low relief with hummocky topography (Figure 1-5) rising to steep hills on the north and south of the catchment. The west boundary of the catchment is a gentle saddle. To the west of this saddle, water drains to the Potts River. The outlet of the catchment, Lambies Stream, is incised into the banks surrounding the eastern edge of Lake Clearwater. The altitude of the Lake is 667 m and the surrounding hilltops are 1300 m. Complex glaciated terrain, made up of glacier deposited alluvial sediments and moraines, dominates the landscape. Glaciated terrain also includes Kettle Holes, Kame Deposits, and other glacial deposits (Evans, 2008). Figure 1-5, Figure 1-8 and Figure 1-9 show the catchment topography.

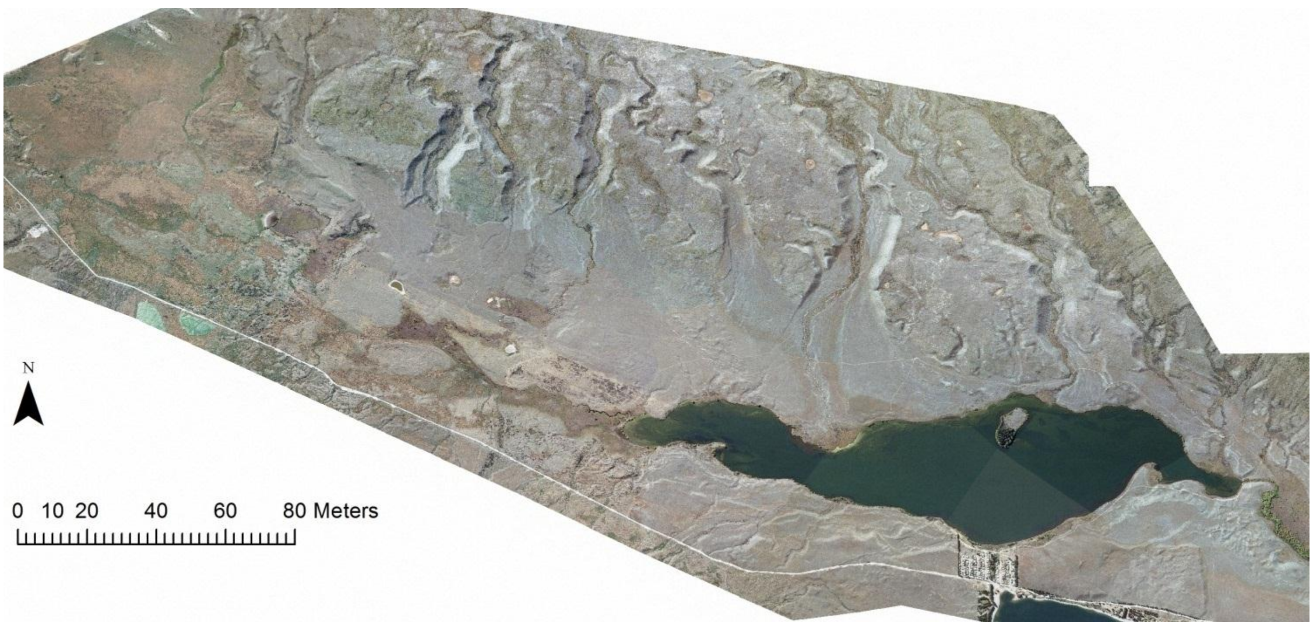

Figure 1-5, Aerial photograph of Lake Clearwater and surrounding landscape

1.6.2 Climate

The Lake Clearwater Catchment (Figure 1-4) is prone to very strong winds and westerly winds carry much of the precipitation for the area (Burrows, 2002). Rainfall is higher in the western areas of the Hakatere area due to the orographic effect of the Southern Alps (Figure 1-6). Rainfall also varies with elevation considerably. Mt Smite (2003 m), which lies roughly 14 km north-northwest of Lake Clearwater, has recorded rainfall of around 1815 mm yr^{-1}, whereas upper Lake Heron (700 m) receives in the vicinity of 1108 mm yr^{-1} (Burrows, 2002). The Hakatere area is estimated have a mean annual potential evapotranspiration (PET) estimated at 800-900 mm yr^{-1} (Figure 1-6).

In summer, the temperature can rise as high as 30°C, and in winter it will be as low as 10 °C to -15 °C (Burrows 2002). Snowfall is common in winter and normally results from southerly weather systems. Snow covers lower elevations of the catchment for no more than 10–20 days each year while the upper elevations can remain covered most of winter. The surface of Lake Clearwater and the wetland often freeze during winter.

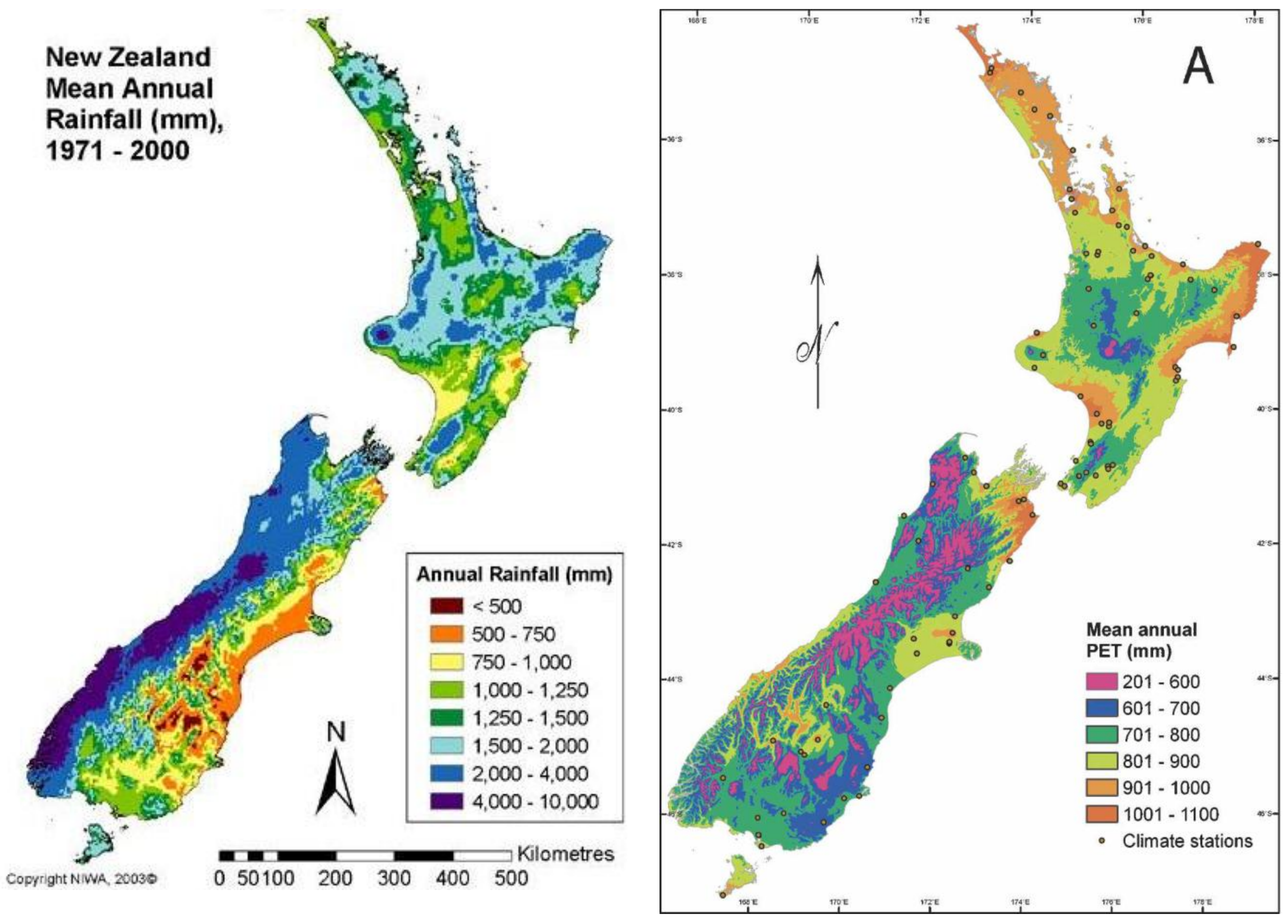

Figure 1-6, Maps of mean annual rainfall and PET in New Zealand (NIWA 2003)

1.6.3 Lake Clearwater

Lake Clearwater is a shallow inter-montane lake formed by glaciation (Evans 2008). The lake is an elongated shape and lies in the base of the main valley (Figure 1-7). It is around 19 m deep at it deepest point. Lake Clearwater is part of the Ashburton Lakes district, a group of lakes recognised for their high diversity of wetland types and plant communities (Winton, 2008). Lake Clearwater is the only major lake in the Clearwater catchment and is 667 m above sea level.

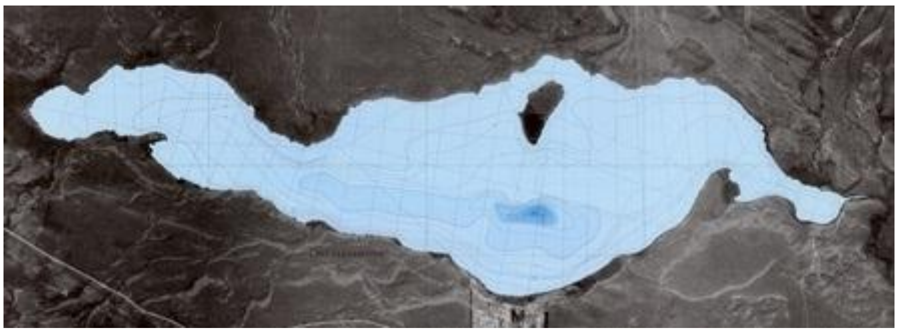

Figure 1-7, Lake Clearwater bathymetry (NIWA 1985)

1.6.4 Wetlands

Wetlands in the Lake Clearwater catchment are largely pristine examples of a native inter-montane wetland system, consisting of ephemeral turfs, streams, swamps and bogs. The wetland vegetation is predominately Red Tussock (*Chionochloa rubra)* and *Carex secta* (Bev Clarkson, personal communication 2011) growing in a peat organic-rich soil, supporting considerable ecological diversity, including native fish, birds and plants (Department of Conservation, 2011).

The main wetland in the catchment runs from the inlet of Lake Clearwater along the valley floor to the catchment boundary. One perennial channel runs through the wetland (Figure 1-8 and Figure 1-9). Craddock Stream flows from the northern hillslope into the western end of the wetland. Upstream Craddock Stream has many small wetlands of a similer type to the main wetland.

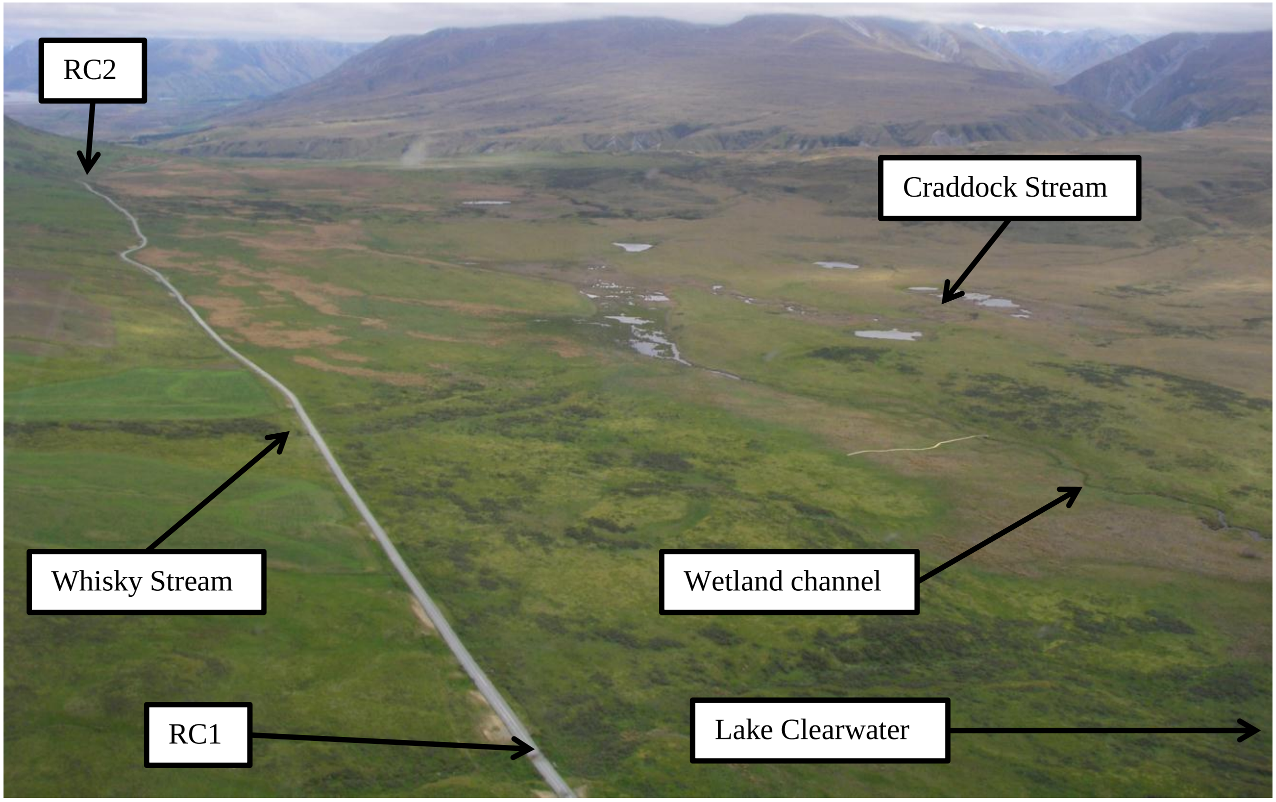

Figure 1-8, Aerial photograph of Whisky Stream and the main wetland channel (Adrian Meredith (ECan))

1.6.5 Streams

Streams in the catchment are shown in Figure 1-9. Whisky Stream is the second perennial tributary flowing into the main wetland. Whisky Stream flows from the southern hillslope through farmed land and into the main wetland channel.

Three streams flow directly into the lake from the north side of the valley; these streams include Craddock Stream and Kenneth Creek. The third stream is an unnamed stream that flows into the eastern end of Lake Clearwater near the lake outlet. This stream runs below Mt Guy and is referred to as Mount Guy Stream in this study. Streams on the northern hillslope have natural tussock grassland catchments.

The west end of the lake is bordered by moraine deposits with a single surface water outlet, Lambies Stream. Lambies Stream flows from the lake outlet and eventually flows into the south branch of the Ashburton/Hakatere River (Section 3.3). The South Ashburton River is an alpine-fed river with mean annual flow of around 577 mm year^{-1}.

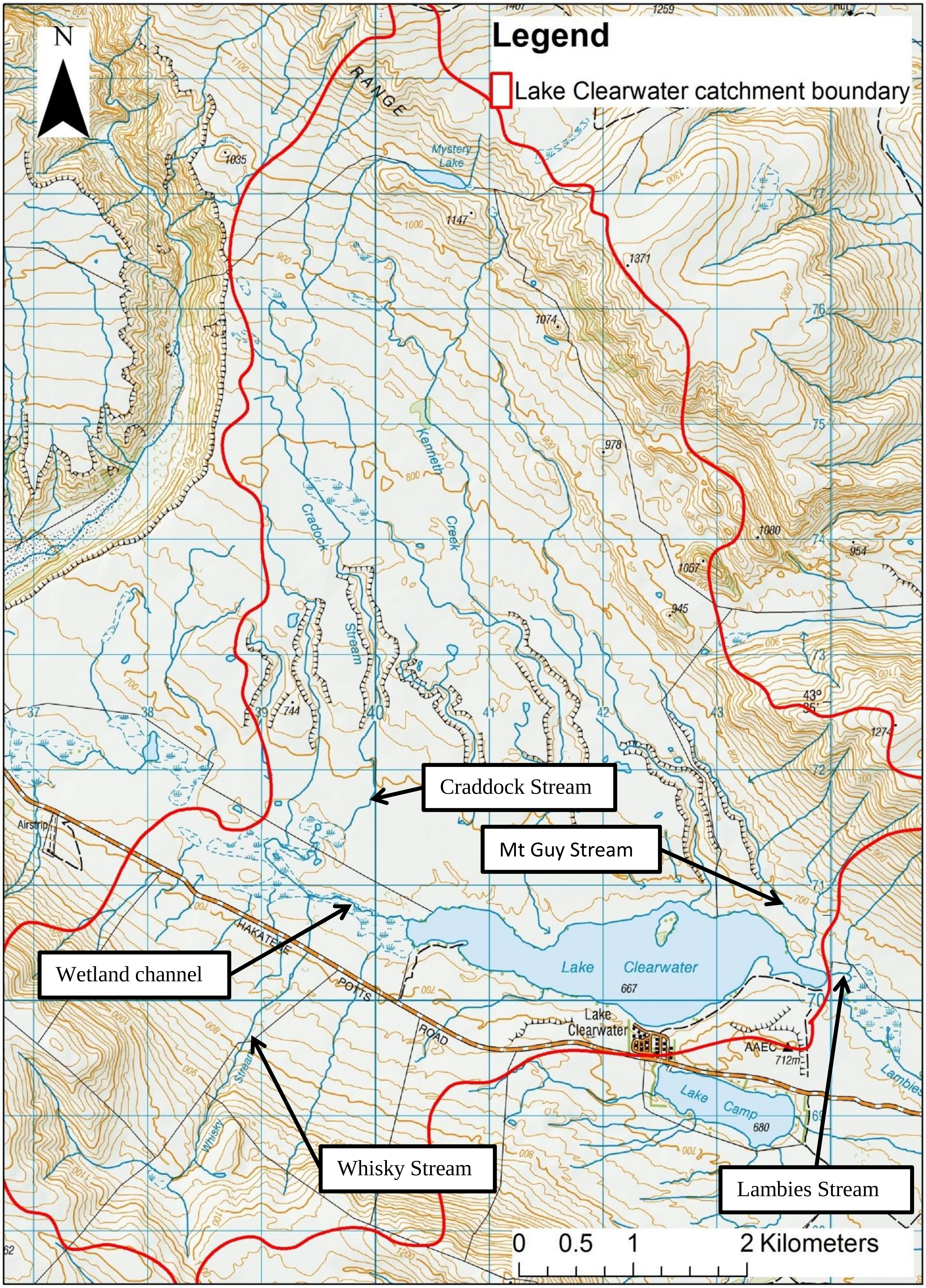

Figure 1-9; Lake Clearwater Catchment NZTopo 50 showing catchment topography and waterways (LINZ, 2009, NIWA, 2010b)

1.6.6 Hydrogeology

Figure 1-10 shows a surface soil layer (0 to 3 metres thick) of bedded silt and fine sand that is present across the Lake Clearwater valley (Evans 2008). In the wetland area, this surface soil is mixed with accumulated organic matter. Below the surface layer is a, 2-meter thick, poorly-sorted fluvial gravel layer (Evans 2008). This layer likely provides a subsurface lateral flow pathway with high hydraulic conductivity. The gravel layer was most likely deposited by water flowing from the Mt Potts River catchment when the Lower Potts Valley was blocked by ice (Evans 2008). Below this is a well-sorted glacially deposited "diamict" layer created by a glacier originating from the Potts River valley. This layer is likely to have relatively low hydraulic conductivity (Stephenson et al. 1998).

Figure 1-10, Photograph of an exposed outcrop in the Potts River valley (Evans 2008)

1.6.7 Land use

The Clearwater Catchment is a tussock and grassland inter-montane basin typical of the Hakatere area. Land to the north of Lake Clearwater is DOC owned and managed and is largely natural. Before 2007, prior to DOC ownership, this area was lightly grazed by pastoral leaseholders (R. Clucas, personal communication, 3rd May 2011). The primary environmental concern is the potential for increased nutrient loads from diffuse sources as agricultural land use (Figure 1-11) becomes more intensive on the south side of the wetland (Sukias et al. 2005, R. Clucas, personal communication, 2-6-2012).

Figure 1-11, Aerial photograph of the farmed hillslope in the Lake Clearwater catchment in 2011 (Adrian Meredith (ECan))

South of lake Clearwater and the wetland, farming has intensified on some freehold land following recent (2007) tenure review and subsequent replacement of grazing land with the Hakatere conservation reserves. Figure 1-11 shows the farmed hillslope within the Lake Clearwater catchment during ploughing in 2011. Ten percent of the total catchment is farmland and the remainder is natural tussock grassland with the exception of a bach community between Lake Clearwater and Lake Camp. A summary of land use for the catchments of each monitored waterway is shown in Table 1-2. Land use information is based on site observations.

Table 1-2, Sub catchment land use summary for monitored waterways

	Whisky Stream	Road Culvert One	Upstream wetland	Main wetland channel	Lake outlet	Mount Guy Stream
Total area (km2)	4.51	0.47	6.56	19.12	46.00	3.65
Farmed (km^2)	0.72	0.36	0.00	2.92	4.18	0.00
Percent farmed (%)	16%	77%	0%	15%	9%	0%

Farming activities are predominantly sheep and beef grazing. In recent years, since 2009, roughly 60% of the farmland in the Lake Clearwater catchment has undergone ploughing and over-sowing with rough pasture or brassica (Figure 1-12).

Figure 1-12, Winter feed growing on farmland in 2012

2 Methods

2.1 Hydrological investigation

2.1.1 Rainfall

Measured rainfall from the Hakatere Remote Automated Weather Station (RAWS) (DOC 2011) operated by DOC was assumed to be representative of the rainfall in the Hakatere area and the Lake Clearwater catchment. The station is 8 km east of the Lake Clearwater outlet (Figure 2-1) and records hourly rainfall (2003-present).

2.1.2 Evaporation and evapotranspiration

The closest evaporation measurement station to the Clearwater catchment is the “Methven CWS” station (NIWA 2012a). This station (latitude -43.63978, longitude 171.65205) is 48 km northeast of the Clearwater catchment and is 313 m above sea level. Daily open water evaporation (calculated using the original Penman method (Environment Canterbury 2012)) and potential evapotranspiration (PET, calculated using the Penman-Monteith method (NIWA 2012b)) was obtained for this station. Evapotranspiration (ET) in the Lake Clearwater catchment may differ from ET in the nearby Canterbury Plains (Figure 1-6) due to altitude, lower temperatures, strong winds and low humidity.

Therefore, PET estimates (calculated using the Penman-Monteith method) were obtained for two Virtual Climate Network Stations (VCNS, (NIWA 2012c) within the Clearwater catchment. One VCNS is near Mt Guy Stream (MGS) (Figure 2-2) (Agent number: 15219) and one is near Whisky Stream (Agent number: 19809). NIWA’s VCN model (NIWA 2011) calculates daily potential evaporation at sites in a virtual 5km grid across New Zealand via interpolation of climatic conditions at real climate stations. The VCN model uses the Penman method to calculate PE as described in Burman and Pochop (1994). The model used to provide PET estimates at VCN sites has an estimated average daily error of 1 mm in summer and 0.4 mm in winter (Tait et al. 2006). Interpolated VCN data for sites above 500 m may be less accurate, however, due to the paucity of measured data from high-elevation sites (Tait and Woods 2007).

Annual open water evaporation depth at Lake Clearwater was estimated by multiplying open water evaporation depth at the Methven CWS weather station by the same percentage as the difference in PET between Methven CWS and the VCN station at MGS (84%). Total evaporation loss from Lake Clearwater was calculated from open water evaporation depth multiplied by the surface area of Lake Clearwater.

2.1.3 Hakatere catchment rainfall and runoff

Annual rainfall and runoff for the Hakatere Basin catchment was used for comparison with runoff estimated in the Lake Clearwater catchment. The annual runoff from the Hakatere catchment was also used to estimate the subsurface flow from the farmed hillslope (Section 0). Runoff was evaluated for the Hakatere Basin using two long-term daily flow-gauging stations in the South Ashburton River. These stations are operated by Environment Canterbury. The catchments, gauging stations and weather station are shown in Figure 2-1.

Table 2-1, South Ashburton River Gauging stations (Gabites 2006)

Site	Site Name	Map Reference	Catchment Area	Date range
68806	South Ashburton River at Mt Somers	K36:7260-2610	539 km^2	1967-Current
68827	South Ashburton River at Buicks Bridge	J36:6141-3450	145 km^2	2002-Current

The assumption was made that all runoff from the South Ashburton River catchment upstream of Buick's Bridge flows through the Buick's Bridge gauging station and that all runoff from the catchment upstream of the Mt Somers gauging station flows through that gauging station. These assumptions are thought to be realistic; however, runoff flowing out of both catchments as unmeasured groundwater is possible.

The catchment upstream of Buicks Bridge has a higher average elevation and is located to the west of the South Ashburton River catchment. As a result, this catchment receives higher rainfall than the Hakatere Basin. Subtracting the flow at Buicks Bridge from the flow at Mt Somers gave a runoff estimate for the remaining catchment upstream of Mt Somers. This catchment is predominantly the Hakatere basin area, which contains the Lake Clearwater catchment. The majority of this catchment has similar topography, land-cover and altitude to the Lake Clearwater Catchment. Rainfall and runoff for the Hakatere basin was calculated for all years with available data (2003-2012). Annual totals were calculated from winter to winter (1st July until 30th June).

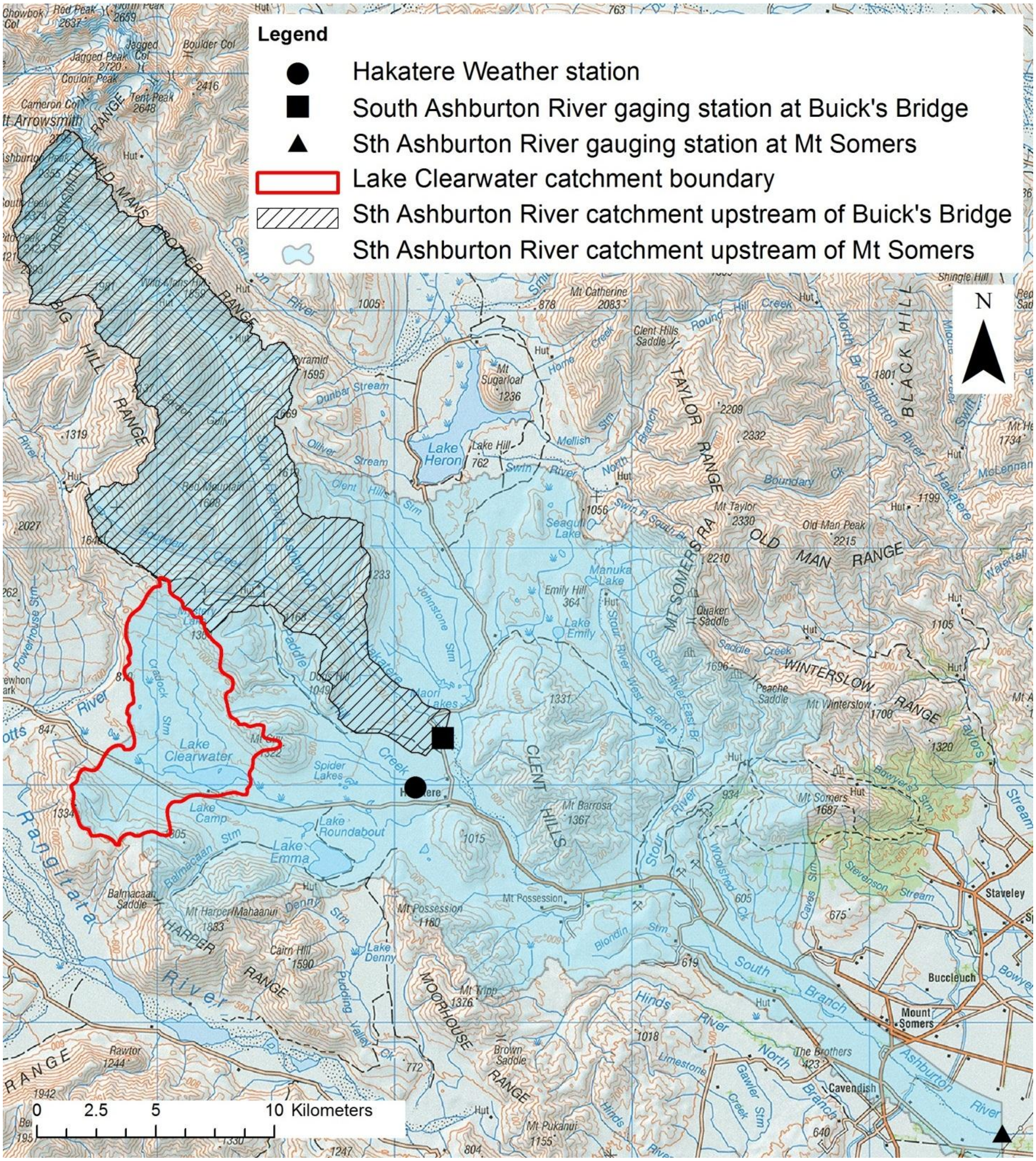

Figure 2-1, Hakatere catchments and gauging stations

2.1.4 Flow monitoring

Flow was monitored at 10 sites in the Clearwater catchment (Figure 2-2). Eight sites used stage-discharge curves to relate stage to flow and two sites used 90^0 v-notch weirs. Stream flow rate was measured using the velocity-area method (Chow et al. 1988) and stage height was plotted against the corresponding measured flow rate to develop a stage-discharge curve. A site description and the coefficient of determination R^2 for the stage-discharge curves is given in Table 2-2.

Table 2-2, Flow monitoring station summary

Site	Waterway type	Channel	Flow type	Flow measurement	R^2
WS1	Perennial stream	Round concrete culvert with stony bottom	Fast flowing and turbulent	Manning's eqn	N/A
WSW	Perennial stream	Weir	N/A	90^0 v-notch weir	N/A
WS2	Perennial stream	Cobbled streambed	Fast flowing and turbulent	Stage-discharge curve	0.905
WS3	Perennial stream	Gravel streambed	Fast flowing and turbulent	Stage-discharge curve	0.778
RC1	Ephemeral stream	Round concrete culvert	Fast flowing and laminar	Manning's eqn	N/A
RC2	Ephemeral stream	Flat bottomed concrete culvert	Fast flowing and laminar	Manning's eqn	N/A
WC1	Perennial Wetland channel	Smooth muddy streambed	Slow laminar flow	Stage-discharge curve	0.886
WC2	Perennial Wetland channel	Muddy stream bed with some stones	Slow laminar flow	Stage-discharge curve	0.916
MGS	Perennial stream	Weir	N/A	90^0 v-notch weir	N/A
LS1	Perennial stream	Smooth mud and gravel stream bed	Slow laminar flow	Stage-discharge curve	0.899

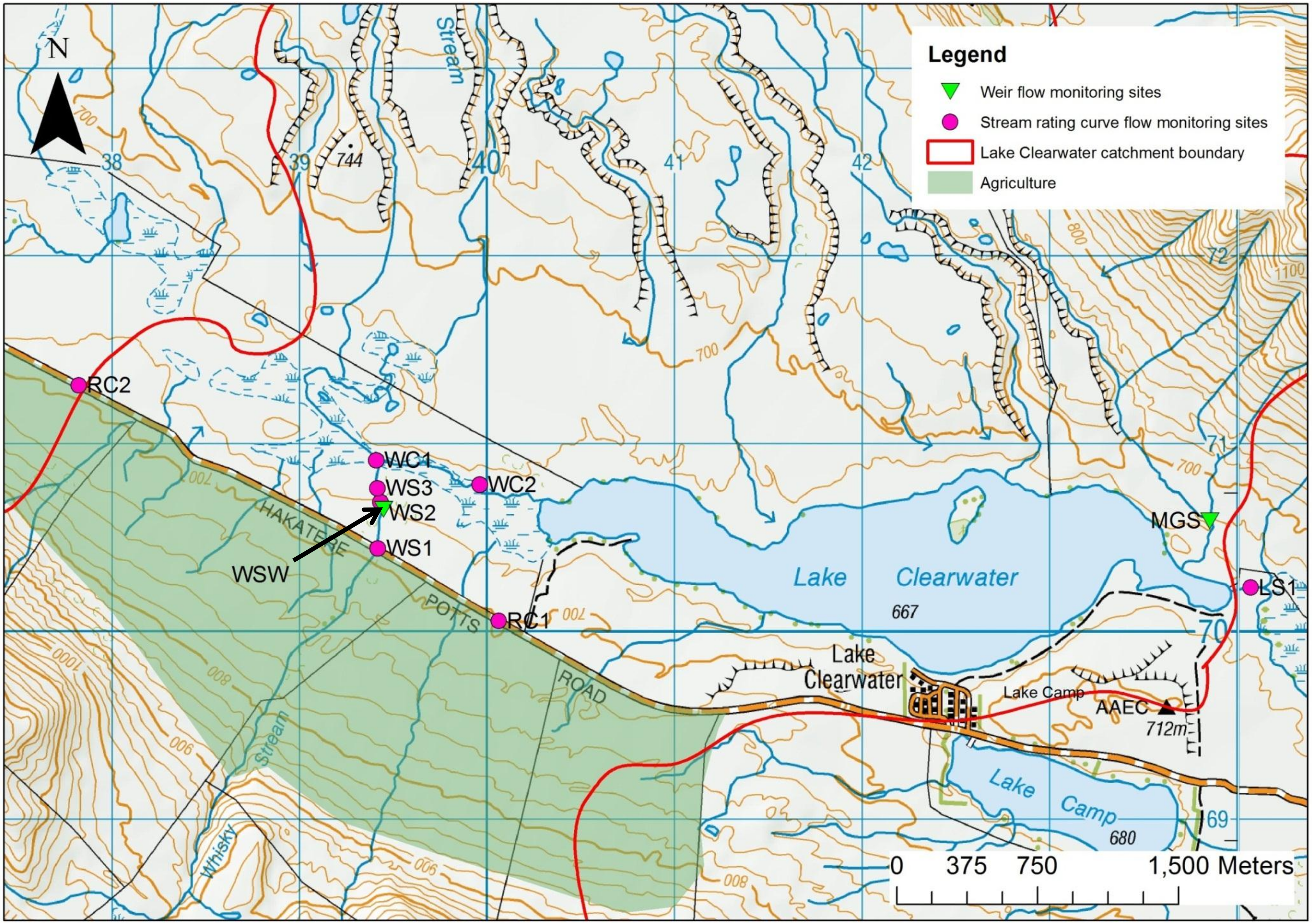

Figure 2-2, Map showing all flow monitoring sites for this study

Odyssey (ODYWL10) water level logging probes were used to record water level throughout the study. Before installation at the field sites, probes were calibrated in tracer mode at two water levels. The water level was entered into the Odyssey software to correspond with the capacitance reading at each level, allowing the programme to create a linear capacitance-depth relationship for each metre. The lake inlet and outlet water level was monitored by Trutrack water level probes installed by DOC. Water level was recorded at 15-minute intervals in Odyssey loggers and 30-min intervals in Trutrack loggers. An Odyssey logger can be seen measuring stage at WC1 in Figure 2-3.

Figure 2-3, Odyssey logger at WC1

Stage discharge curves were used to calculate flow rate from stage height measurements. The stage discharge curves (SDC) for WS2 is shown in Figure 2-4. WS2 and WS3 are natural channels with a cobbled streambed and turbulent riffles. A combination of relationships was used to calculate flow from stage at WS2. This improved agreement, compared to both linear and power relationships, between WS2 flow and WSW flow. Below 0.215 m, a power curve was used to avoid predicting zero flow during low flows. Above 0.215 m, a linear relationship was used to avoid over prediction of high flows. Seasonal vegetation and flood debris in the channel immediately downstream of WS2 stage measurements changed the channel sufficiently to cause flow-gauging measurements from 2010 to be unreliable. Therefore, only five flow measurements from 2011 are used for this rating curve (Figure 2-4).

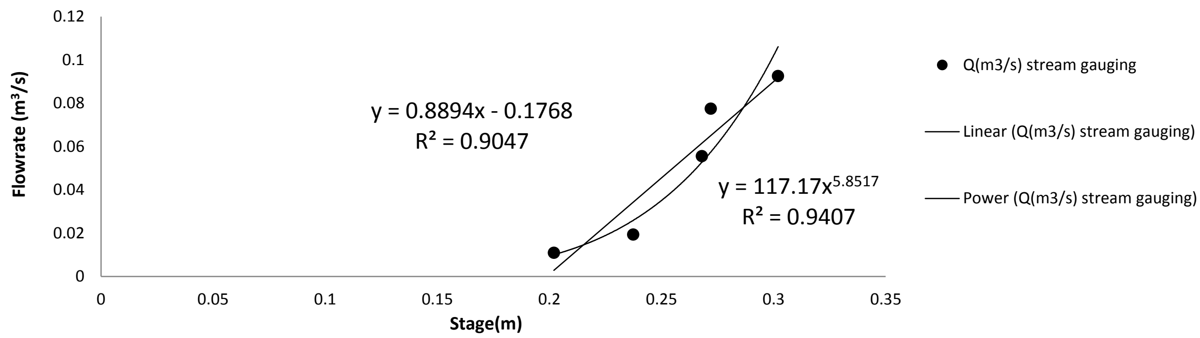

Figure 2-4, WS2 stage discharge curve

The SDC used to evaluate flow at WS3 is shown in Figure 2-5. This site was thought to be the most reliable method for annual flow estimates in Whisky stream. Of all the sites in Whisky Stream, the stream channel at WS3 was the most suited for gauging. This was due to a relatively smooth and even streambed and less turbulent flow conditions. A linear relationship was used as it gave a better fit to the data than a power relationship.

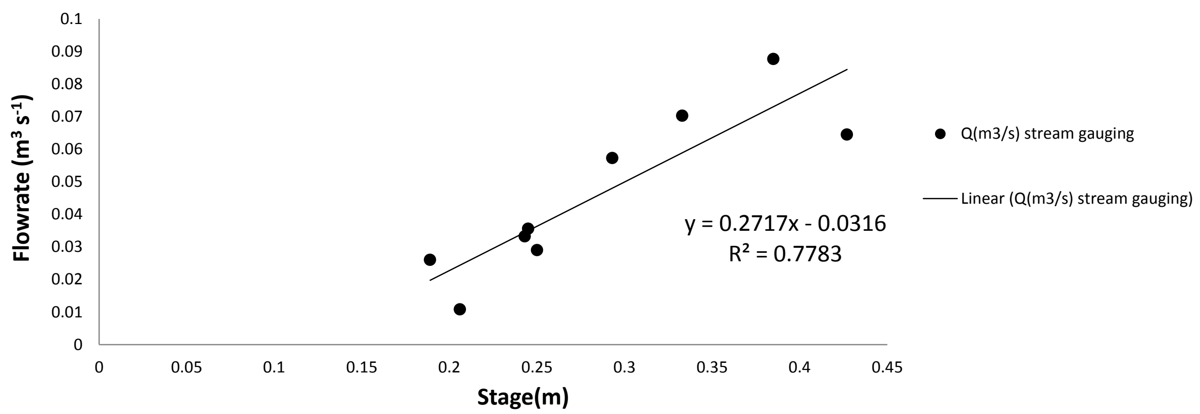

Figure 2-5, WS3 stage discharge curve

The SDC used to evaluate flow at WC1 is shown in Figure 2-6. A power relationship is used for this site as it provided the best fit to the data. The power curve is appropriate for this site, as the cross-sectional area of the channel increases rapidly with higher stage and flow rate was expected to increase more per unit of stage at higher flows. This site was thought to be the most reliable for annual estimates of flow in the wetland channel. USW is not monitored for flow, as it was not included in the original network of monitoring locations. Annual runoff yield for USW was assumed to be the same as WC1 to allow loading to be estimated at USW.

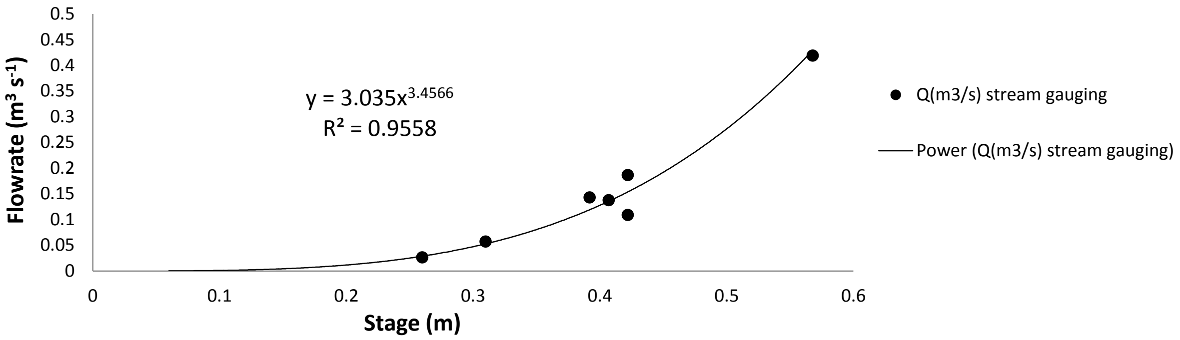

Figure 2-6, WC1 stage discharge curve

The SDC used to evaluate flow at WC2 is shown in Figure 2-7. A linear relationship was used for this site as it provided the best fit to the data. WC2 was moved upstream in early 2011 to improve the accuracy of flow gauging measurements. Therefore, gauging data is limited at this site as flow measurements taken in 2010 were for a location further downstream. Monitoring was also disrupted due to logger probe failure in October 2011. Very slow flow velocity at this site increased uncertainty in flow rate estimates and backwater effects from the lake are likely to have changed the stage discharge relationship during high lake levels. Because of this flow, data from WC2 was less accurate and was not used.

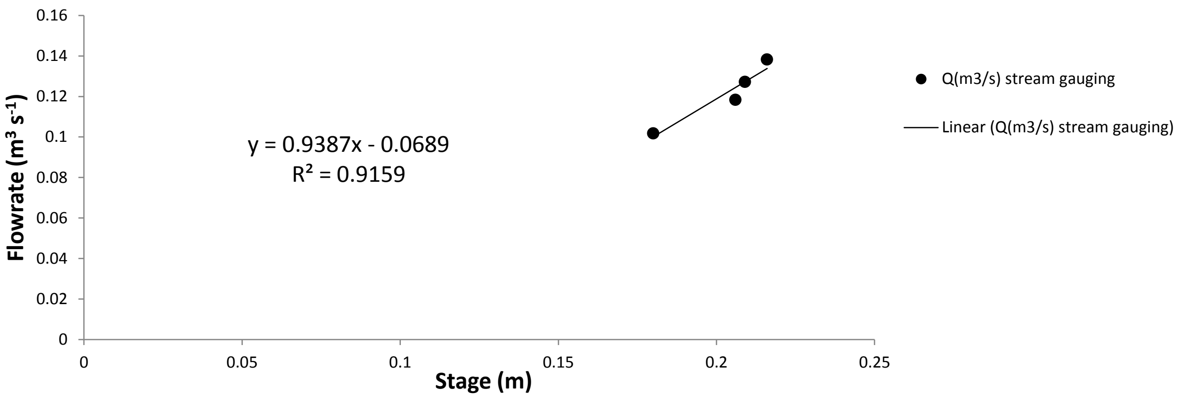

Figure 2-7, WC2 stage discharge curve

The SDC used to evaluate flow at LS1, the lake outlet, is shown in Figure 2-8. Flow velocity was very slow at low flows and was a source of uncertainty in flow rate measurements. However, the channel at LS1 was uniform and well suited to stream gauging measurements. The channel also had a large cross-sectional area allowing more measurements to be taken across the width of the stream compared to smaller streams at the other gauging sites in this study. This decreased uncertainty in cross-sectional area and flow velocity.

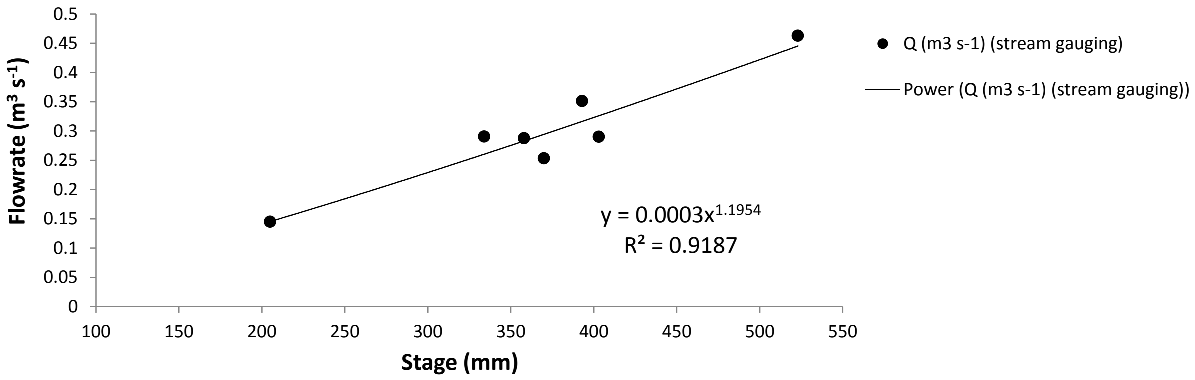

Figure 2-8, LS1 stream rating curve

Flow measurement for RC1 utilized the culvert beneath the Hakatere-Potts Road. Dimensions, slope (S) and roughness (n) of the wetted surface in the culvert were used to estimate flow velocity (V) using Manning's equation (2-1) (Chow et al. 1988). The coefficients of roughness were estimated by visual inspection of the culvert wetted surface and comparison to standard charts in Chow et al (1988). The coefficient of roughness used for RC1 was 0.15. R is the hydraulic radius.

$$V = \frac{R^{2/3} S^{1/2}}{n} \tag{2-1}$$

Flow was found from the calculated average velocity using the Manning's equation multiplied by the cross-sectional area ($A_{Culvert}$) of the water in the culvert. Cross-sectional area was calculated from the height (h) of water in the culvert via equation (**2-2**. r is the radius of the culvert.

$$A_{culvert} = r^2 cos^{-1}\left(\frac{r-h}{r}\right) - (r-h)\sqrt{2rh - h^2} \tag{2-2}$$

Due to backwater effects, the stage recorded by the stage logger at RC1 was not representative of water depth in the culvert and a reliable estimate of flow could not be made from stage logger data. Therefore, annual runoff for RC1 was estimated using a linear relationship between flow rates at RC1 and WS3. Seven manual measurements of flow at RC1 were plotted against flow in WS3 measured at the same time. The resultant linear equation was used to calculate flow at RC1 from WS3 stage data.

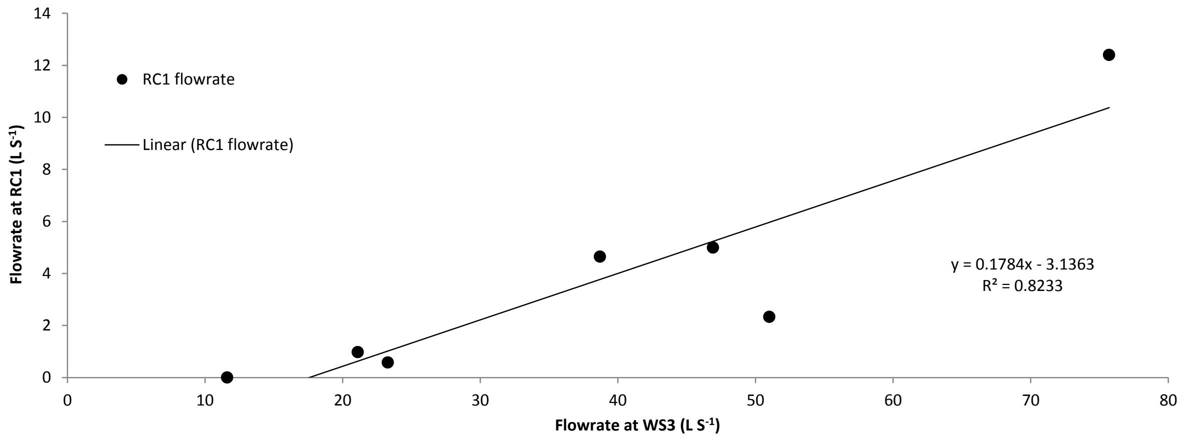

Figure 2-9, Scatter plot of flow at RC1 against flow at WS3

Weirs were installed at MGS and WSW sites (Figure 2-10) to provide more accurate flow gauging. Weirs were sharp crested 90^0 v-notch weirs designed and installed as per guidelines in the United States Geological Survey's water supply paper 2175 (U. S. Geological Survey 2005). The stage discharge relationship for the weir is shown in equation (2-3. Flow (Q) is calculated as a function of the height (h) of the water above the base of the weir v-notch.

$$Q = 1.36h^{2.48} \tag{2-3}$$

Figure 2-10, V-notch weirs at MGS (left) and WSW.

The MGS weir was installed 14th August 2011. To obtain a complete annual flow record, monthly total runoff for July and August 2011 at MGS was estimated from a linear relationship between runoff at WS2 and MGS (Figure 2-11).

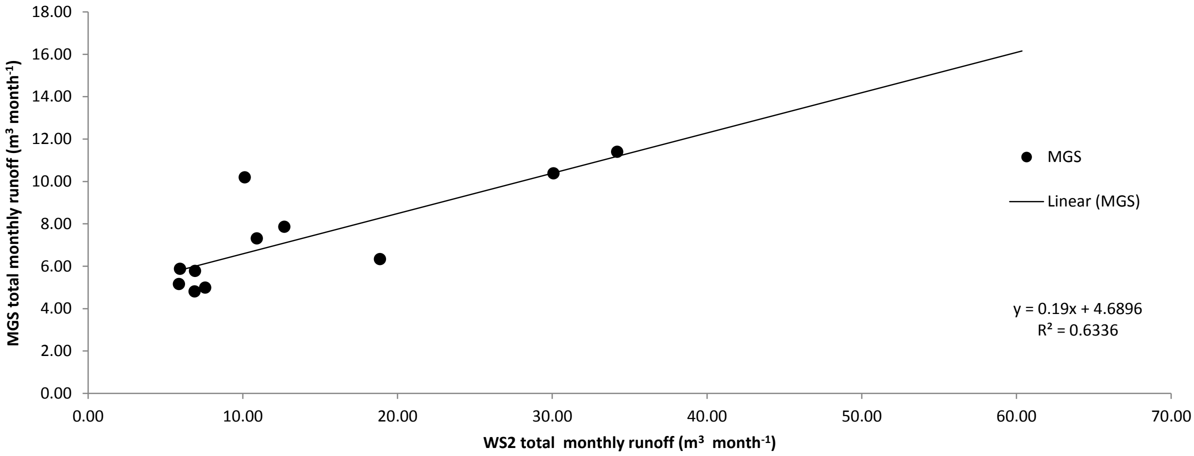

Figure 2-11, WS2 versus MGS total monthly runoff

2.2 Water balance

An annual water balance was used to estimate the volume of subsurface throughflow runoff from the farmed hill slope. Components of the water balance are shown in (2-4).

$$P = ET + R_S + R_G \quad (2\text{-}4)$$

Water enters the balance as precipitation (P) and is lost by evapotranspiration (ET), surface water runoff (R_S) and subsurface runoff (R_G). Losses to deep groundwater are assumed negligible.

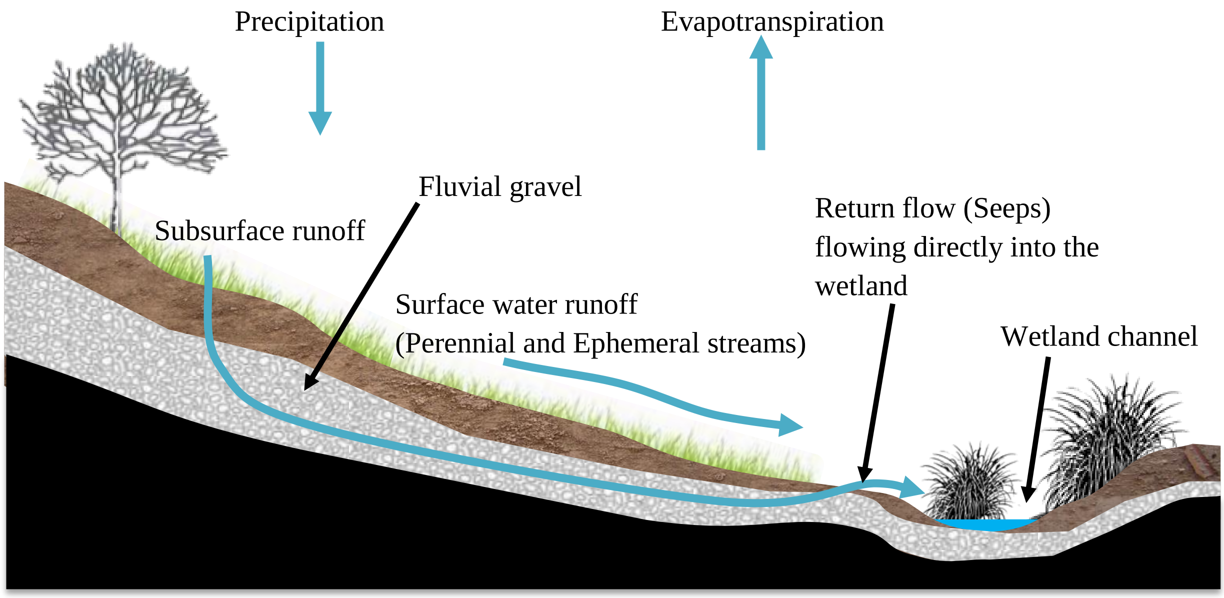

Figure 2-12, Hillslope water balance components

Total annual subsurface water runoff (R_G) from the farmed hillslope, for 2011-2012, was calculated using a simplified water balance (2-5). R_S was estimated from flow measurements of surface water from Whisky Stream. Total runoff depth for 2011-2012 from the farmed hillslope was assumed the same as total runoff depth from the Hakatere catchment (R_H) (Section 2.1.3). Surface water runoff was then subtracted from total runoff to provide an estimate of annual subsurface runoff (2-5).

$$R_G = R_H - R_S \quad (2\text{-}5)$$

2.3 Subsurface flow estimation using Darcy's equation

An estimate of possible subsurface runoff lateral velocity was also made using Darcy's equation (2-6).

$$v = -K\frac{\Delta h}{\Delta l} \qquad \textbf{(2-6)}$$

The groundwater table was assumed to be parallel to topography. Therefore, change in height of the water table from the farmed land to the wetland channel (Δh) can be estimated to be 30 metres. The subsurface flow was assumed to be parallel to the hillslope. This allowed the average length of the subsurface runoff flow path (Δl), from the farmed land to the wetland, to be estimated at 400 metres.

No aquifer tests or water table measurements were possible because shallow boreholes could not be excavated with a portable powered soil auger. A stony layer prevented drilling of boreholes deeper than 0.5 metres. Boreholes were attempted at five sites. At all sites, the stony layer was no deeper than 0.5 m. Groundwater levels were below the depth reached at all borehole locations. A 2-metre thick glacial-fluvial gravel layer (Figure 1-10) was assumed responsible for the majority of subsurface lateral flow (Figure 2-12). This layer was assumed to be widespread across the Lake Clearwater catchment including beneath the farmed hillslope. This assumption was supported by the observation of an obvious gravel layer, 0.5 metres below the surface, at all locations below the farmed hillslope where manual drilling of shallow boreholes was attempted. In addition, all seeps were observed to have a bed of gravel similar in appearance to the fluvial layer shown in Figure 1-10. Hydraulic conductivity is estimated from literature values for glacial fluvial gravel in Stephenson et al. (1998). The flow velocity (v) in was calculated for a high (4250 mm hour^{-1}), low (0.42 mm hour^{-1}) and mid (42.5 mm hour^{-}1) value of hydraulic conductivity.

Subsurface runoff volume was estimated using equation 2-7. Length of the farmed hillslope (L) perpendicular to the direction of flow was estimated to be 2000 metres. Thickness of the gravel layer (H) was assumed to be 2 metres thick based on observations in Evans (2008) (Figure 1-10).

$$Q = v \times L \times H \qquad \textbf{(2-7)}$$

2.4 WATYield model

The WATYield model was designed to predict runoff from measured rainfall and PET, and has been used in a number of catchments in NZ (Fahey et al. 2004). Knowledge of each physical hydrological process is in the form of equations and parameters and knowledge of the stochastic hydrological environment is supplied to the model as hourly rainfall and PET depth. The original model calculated runoff in a daily time step from daily rainfall and PET depth. The model was modified, in this study, to estimate water balance parameters, such as actual evapotranspiration and surface water runoff, for the Whisky Stream catchment on an hourly time scale, and was also intended to provide runoff estimates for ungauged sub catchments within the Lake Clearwater catchment. The model was modified for use in this study in MATLAB, a numerical computing programme.

For all model runs, hourly rainfall from the Hakatere RAWS rainfall station was used. The model was run for two years from July 2010 until June 2012. Whisky Stream VCN station data was used for daily estimates of PET. Daily PET data was split into hourly fractions based on data in Oliphant et al. (2003). A unit hydrograph convolution (Mosley et al. 2004) was added to mimic quickflow response from rain events The unit hydrograph was derived from flow data from Whisky Stream.

2.5 Water quality

Surface water and groundwater seeps were sampled to estimate representative concentrations for each of the key nutrients and to determine nutrient loads within the Lake Clearwater catchment.

2.5.1 Sampling

Grab samples were taken to evaluate instantaneous nutrient concentration at each site. Where possible, samples were taken across all sites for each sampling event to evaluate instantaneous spatial variability. Sampling events were spread randomly over different seasons from May 2010 until July 2012 to capture temporal and spatial variability (Table 2-3).

Figure 2-13 shows the sampling sites along with the agricultural land area and the Lake Clearwater catchment boundary. Whisky Stream and subsurface seep sites are labelled in Figure 2-14 on an infrared aerial image to highlight waterways, topography and vegetation.

Table 2-3, Table showing the date and number of grab samples at each site

	Whisky Stream			Ephemeral channels (Culverts)		Subsurface lateral flow			Upper wetland channel	Main wetland channel		Lake outlet	Control stream
	WS1	**WS2**	**WS3**	**RC1**	**RC2**	**S1**	**S4**	**S5**	**USW**	**WC1**	**WC2**	**LS1**	**MGS**
25 May 2010	x		x	x						x	x	x	x
19 July 2010	x	x	x	x	x					x	x	x	x
9 August 2010	x	x	x	x	x					x	x	x	x
1 September 2011	x	x	x	x						x	x	x	x
19 November 2011	x	x	x	x					x	x	x	x	x
21 November 2011		x											
22 November 2011		x											
15 March 2012	x	x	x			x			x	x	x	x	x
11 April 2012	x	x	x			x			x	x	x	x	x
1 May 2012						x							
11 May 2012						x	x	x					
14 June 2012	x	x	x		x	x	x	x	x	x	x	x	x
Total Number of samples	8	9	8	5	3	5	2	2	4	8	8	8	8

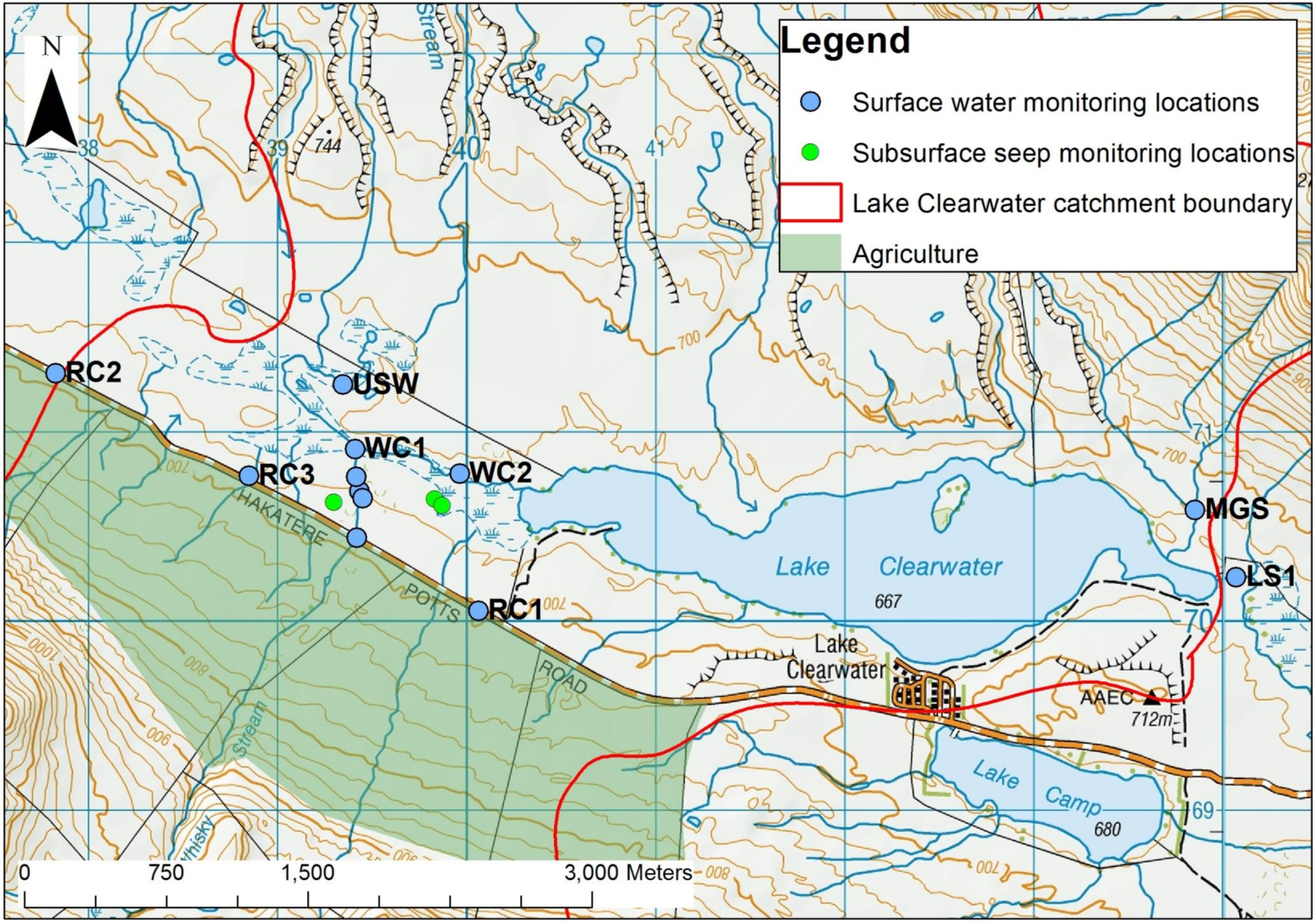

Figure 2-13, Water quality sampling locations used in this study. Whisky Stream, wetland channel and subsurface seep sites are fully labelled in Figure 2-14

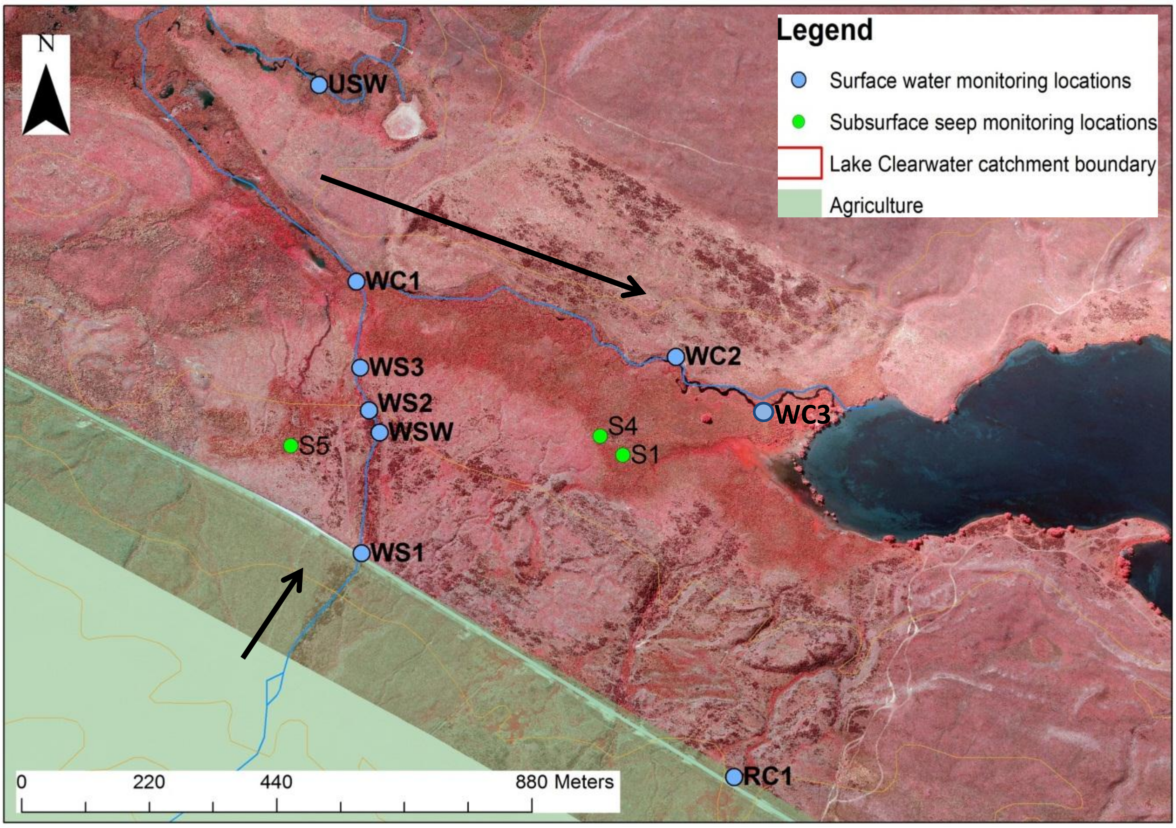

Figure 2-14, Whisky Stream and subsurface seep water quality sampling locations used in this study (Black arrows indicate flow direction).

Storm events can mobilise large quantities of sediment and nutrients into surface waters due to higher flow velocities. It is particularly important to sample storm events as elevated flow during storms has been shown to contribute a large proportion of total annual sediment and nutrient load (Caruso, 2000b, Harding, et al., 2004, Elliott and Sorrell 2002). Therefore, a temporal composite sample was taken at WS2 using an ISCO 6712C automatic sampler. The composite sample consisted of 18 samples taken over time by the automatic sampler (combined into one sample). The sampler was triggered by a 20 mm rise in water level upstream of the Whisky Stream weir. This corresponded to an increase in flow rate from 25 l s^{-1} to 50 l s^{-1}. Eighteen 500 ml samples were taken at 1-hour intervals during a large storm event on the 21st of November 2011 (Figure 2-15). Samples were taken in accordance with QA/QC (section 2.5.2).

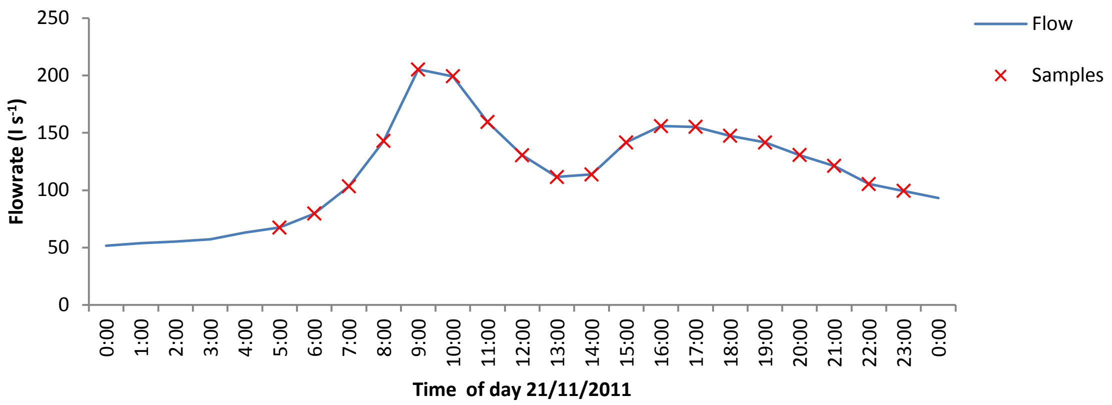

Figure 2-15, Timing of automatic samples taken during a storm event on 21st of November 2011

The 18 samples were measured individually for specific conductance. Samples were then combined to provide a composite sample. A composite sample was used, as the cost of analysis for 18 samples was beyond the budget for this study. The composite sample provided average concentration over the storm event. This provided a representative concentration for a high flow event. However, concentration is likely to be subject to rapid and significant changes over the course of a storm event.

2.5.1.1 Surface water sampling sites

Two un-impacted sites where chosen (MGS and USW) as relevant reference sites, from which a comparison to impacted sites could be made. USW is a wetland site upstream of any potential farm impacts and MGS is a site in Mt Guy Stream, which drains conservation land. Both sites are located on the north side of the lake and wetland.

Three sites (WS1, 2 and 3) formed a transect along the portion of Whisky Stream that runs between the farmland and the wetland channel. The Whisky Stream Weir site (WSW) was used for flow monitoring only. Whisky Stream is the only perennial stream that flows through the farmed hillslope and farmed area that makes up 16% of the Whisky Stream catchment (Figure 2-16).

Road culvert one (RC1) and road culvert two (RC2) are located in ephemeral streams draining the farmed hillslope catchments (both approximately 80% farmed). The catchment for RC1 is shown in Figure 2-16. Both sites are at the downstream end of concrete culverts under the Hakatere-Potts Road. RC1 enters the main wetland just before the inlet to Lake Clearwater. RC2 flows into a wetland system that drains to the Potts River west of the Lake Clearwater catchment. RC2 is outside the Lake Clearwater Catchment and drains to Mt Potts but is considered representative of ephemeral flow from farmland within the Lake Clearwater catchment.

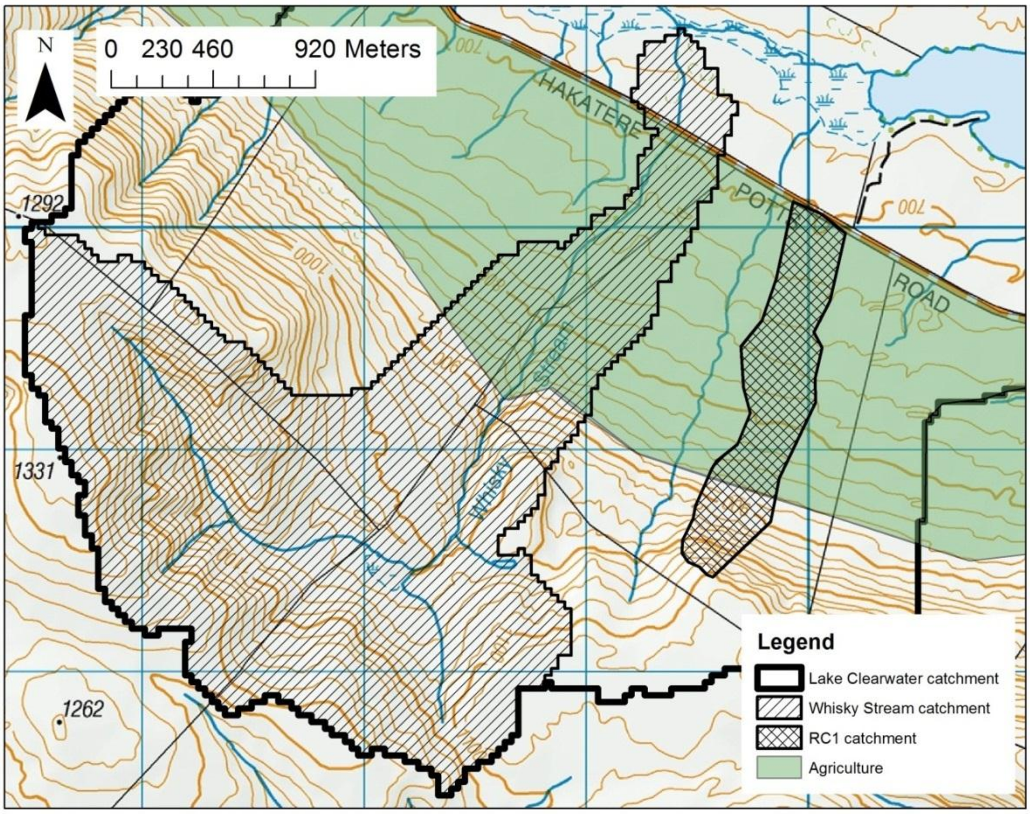

Figure 2-16, Whisky Stream and RC1 catchments

Three sampling locations (WC1-3) were located in the main wetland channel running parallel to the farmed hill slope in the valley floor. WC3 was located 50 metres downstream of WC2 but was replaced by WC2 in 2011 to improve the flow monitoring in the wetland. Whisky Stream and all farmland ephemeral streams drain into the wetland channel and flow to the lake.

2.5.1.2 Subsurface runoff sampling

For this study, it was initially intended to monitor subsurface water quality by sampling from a series of piezometers. However, piezometer installation was not possible with a portable powered soil auger. A stony layer prevented drilling of boreholes deeper than 0.5 metres. Boreholes were attempted at five sites. At all sites, the stony layer was no deeper than 0.5 m. Groundwater levels were below the depth reached at all borehole locations making it impractical to install piezometers in the catchment. This also prevented groundwater table level measurements.

To measure nutrient concentrations in subsurface flow down gradient of the farmland, samples were taken directly from small subsurface seeps. Seep one (S1) was located during a dry period in March 2012. Two more suitable seeps (S4 and S5), below the farmed hillslope, were found in April 2012. No seep could be located draining un-impacted catchments in the Clearwater catchment. An un-impacted seep would have been useful as a control site for subsurface flow.

2.5.2 Quality assurance and quality control

In-situ field meters were calibrated the same day before use in the field as per YSI specifications. Measurements were taken midstream and readings allowed to stabilize. Dissolved oxygen probes were moved through the water when flow was not sufficient to avoid measurement error from oxygen consumption at the electrode. Atmospheric pressure change with altitude was accounted for in field meter calibration.

During nutrient sampling samples were collected in two containers, an unpreserved 1000 ml bottle and a sulphuric acid preserved 250 ml bottle, filled leaving no headspace as per American Public Health Association (APHA) 4500 sampling methods (APHA 1992). All samples were delivered to the lab within 24 hours of the sample being taken and stored in polystyrene bins to avoid high sample temperatures during transport. These tests were performed by Hill Laboratories, an accredited laboratory.

2.5.3 *In-situ* water quality parameters

For each sample *in-situ* measurements of pH, dissolved oxygen, temperature and specific conductance, were made using calibrated YSI field meters (Table 2-4).

Table 2-4, Field meters used to measure in-situ parameters

Parameter	Model of instrument	Units	Range
Dissolved oxygen	YSI 550A	mg L^{-1}	0-50 mg L^{-1}
Specific conductance	YSI 30	µs cm^{-1}	0-499.9 µs cm^{-1}
pH	YSI 60	pH units	pH 0-14
Temperature	YSI 30	^{o}C	0-50 ^{o}C

DO is essential for aquatic life and low DO can indicate degraded water quality. DO was measured during sampling as a parameter to assess the waterway's ability to support aquatic life. DO was also measured to indicate the redox conditions at the time of sampling. Redox conditions in water can affect nutrient cycling, especially denitrification in wetlands.

Specific conductance (SC) was measured as a potential indicator of total dissolved solids content, including dissolved forms of nutrients. pH can affect solubility and speciation of compounds which can affect their bioavailability (Harding et al. 2004). pH can also indicate water quality issues if water is has very low or high pH. Temperature was useful as an indicator of water source. Temperature will also control the rate of chemical and biochemical nutrient cycling reactions in waterways.

2.5.4 Nutrient analysis

Water samples were tested for nutrients of interest including total nitrogen (TN), nitrate + nitrite nitrogen (NNN), total Kjeldahl nitrogen (TKN), ammoniacal nitrogen (NH_4), total phosphorus (TP) and dissolved reactive phosphorus (DRP). Total suspended solids (TSS) were also measured. These tests were performed by Hill Laboratory in Christchurch. Appendix A contains a brief description of the methods used in the analysis of samples.

2.5.5 Non-detects

A non-detect in this study was an analyte concentration below the Hill Laboratory detection limit. To account for non-detects of TN and TP in samples, robust regression on order statistics (ROS) was used (Helsel 2005). A log normal distribution of concentration was assumed to predict concentration values for non-detects. This distribution was shown to fit TN and TP concentration well for sites with few non-detects. This method performs well for small samples numbers (section 2.5.1) with a large number of non-detects (Helsel 2005) and should remove the majority of any bias in the estimation of median values due to non-detects. Lognormal plots showing the results from this method are shown in Appendix B.

2.6 Nutrient loading balance

2.6.1 Catchment loadings

Surface water loading of TN and TP was calculated for the catchments shown in Figure 2-17. Annual loading at each catchment outlet (L_A) was calculated from the product of annual runoff in 2011-2012 (R_S) and median nutrient concentration for all samples (C_{Median}) (2-8). The median concentration was used for the calculation of loads because investigation of the relationship between nutrient concentration and flow in Whisky Stream did not show a clear correlation.

$$L_A = R_S \times C_{Median} \tag{2-8}$$

Annual nutrient yield from natural land (Y_N) was calculated to account for loading from non-farmed land in partially farmed catchments. The product of runoff in each catchment (R_{MGS} and R_{USW}) and median nutrient concentrations for each site (C_{MGS} and C_{USW}) is divided by the area of each catchment (A_{MGS} and A_{USW}). This provides low (Y_{Nlow}) and high (Y_{Nhigh}) estimates of nutrient yield from natural tussock grassland in the catchment 2-9 and 2-10.

$$Y_{Nlow} = \frac{R_{MGS} \times C_{MGS}}{A_{MGS}} \tag{2-9}$$

$$Y_{Nhigh} = \frac{R_{USW} \times C_{USW}}{A_{USW}} \tag{2-10}$$

The high and low estimates of yield from natural land were multiplied by natural land area in partially farmed catchment to calculate nutrient load from natural land in each partially farmed catchments. The high and the low estimate of nutrient load from natural land were subtracted from annual measured in-stream loading at each catchment outlet. The remaining load was attributed to the farmland in each catchment. The yield for farmland in each catchment (Y) was calculated by dividing the load attributed to farmland (L_F) by the farmland area in each catchment (A_F) (2-11).

$$Y = \frac{L_F}{A_F} \tag{2-11}$$

Annual nutrient load in ephemeral runoff from RC2 could not be estimated due to difficulties with flow measurement. Much of the flow escaped from the base of the culvert meaning stage data from the logger was not representative of stage in the culvert. Therefore, annual flow in the ephemeral RC1 catchment was assumed representative of runoff for all ephemeral catchments on the farmed hillslope. Load in the upstream wetland channel was estimated using concentration data measured at this site. However, annual runoff depth at USW was assumed the same as runoff at WC1 to allow a loading estimate to be made. Load from farmland that drained directly into the lake was estimated by using the total yield calculated for farmland in the wetland channel catchment. Loading from unmonitored unfarmed catchments was estimated using yield estimates for natural catchments (MGS and USW).

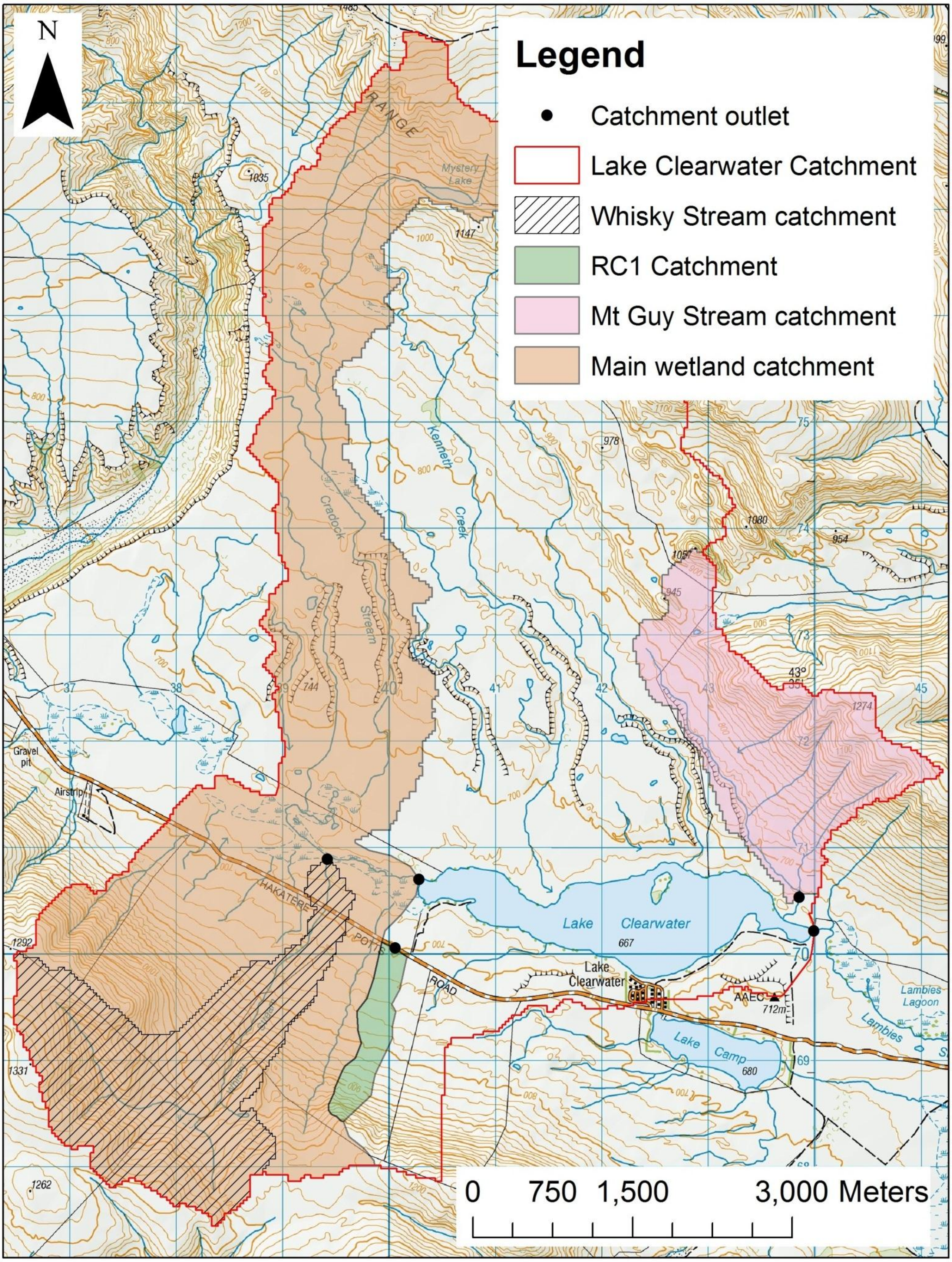

Figure 2-17, Catchments used to calculate surface water nutrient loading

2.6.2 Annual nutrient balance

An annual nutrient balance was calculated for nutrient sources in the wetland channel catchment to estimate subsurface nutrient load. Nutrient loads attributed to farming (L_F) from Whisky Stream and ephemeral catchments on the farmed hillslope were subtracted from the load attributed to farming in the wetland channel (2-12). The remaining unaccounted for load was taken as a loading estimate for subsurface runoff from the farmed hill slope catchment (Figure 2-18).

$$L_{F\ (Subsurface\ runoff)} = L_{F\ (Wetland\ Channel)} - L_{F\ (Whisky\ Stream)} - L_{F\ (Ephemeral\ runoff)} \qquad \textbf{(2-12)}$$

The nutrient yield for subsurface runoff from the farmed hillslope was calculated by dividing the subsurface load by the agricultural area in the wetland catchment. The subsurface runoff was calculated by dividing the subsurface load by the median concentration of TN and TP found at seep locations.

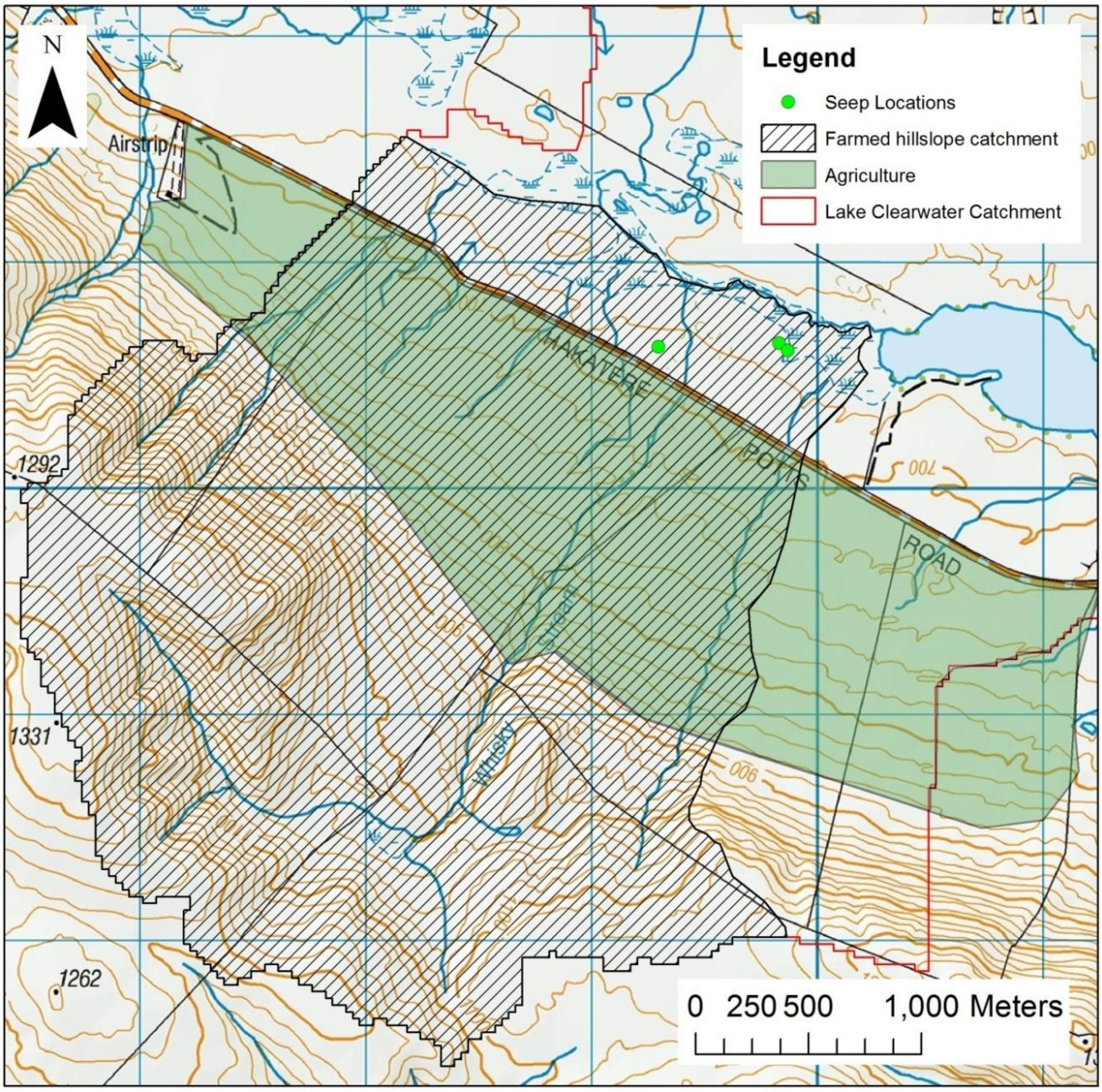

Figure 2-18, Map showing catchment used for subsurface runoff from the farmed hill slope.

2.6.3 Instantaneous nutrient balance

Instantaneous load at each location (L) was calculated as the product of grab sample concentration (C) and flow rate (Q) at the time of sampling.

$$L = C \times Q \tag{2-13}$$

Approximate flow at USW (Q_{USW}), at the time of sampling, was estimated as a proportion of flow at WC1 (Q_{WC1}) using the proportion of catchment area of USW (A_{USW}) and WC1 (A_{WC1}) (2-14).

$$Q_{USW} = Q_{WC1} \times \frac{A_{USW}}{A_{WC1}} \tag{2-14}$$

Approximate runoff from ephemeral catchments (R_E) in the farmed hillslope catchment, at the time of sampling, was calculated by multiplying the runoff at RC1 (R_{RC1}) by the proportion of the catchment area of RC1 (A_{RC1}) and the total farmed ephemeral catchment area in the wetland channel catchment (A_E) (2-15).

$$Q_E = Q_{RC1} \times \frac{A_E}{A_{RC1}} \tag{2-15}$$

2.7 Catchment Land Use for Environmental Sustainability (CLUES) model

The default CLUES model requires no user inputs to run. However, changes were made to the model inputs in this study to improve predictions of loads from the model.

2.7.1 Land use

Land use is a key input to the CLUES model. Each land use has associated source coefficients used to calculate TN and TP load from diffuse sources in each catchment. The derivation of the default land use layer for New Zealand is explained in Elliot et al (2005). The default land use scenario provided in CLUES is shown on the left in Figure 2-19. The land use input layer was modified to reflect current land use, (hill country sheep and beef farming in the area shown on the right in Figure 2-19 and un-grazed tussock grassland in the remainder of the catchment). The proportion of each land use was modified manually for each sub-catchment in the attribute table to match actual current land use in the catchment. No other input parameters for the calculation of TN loads were changed.

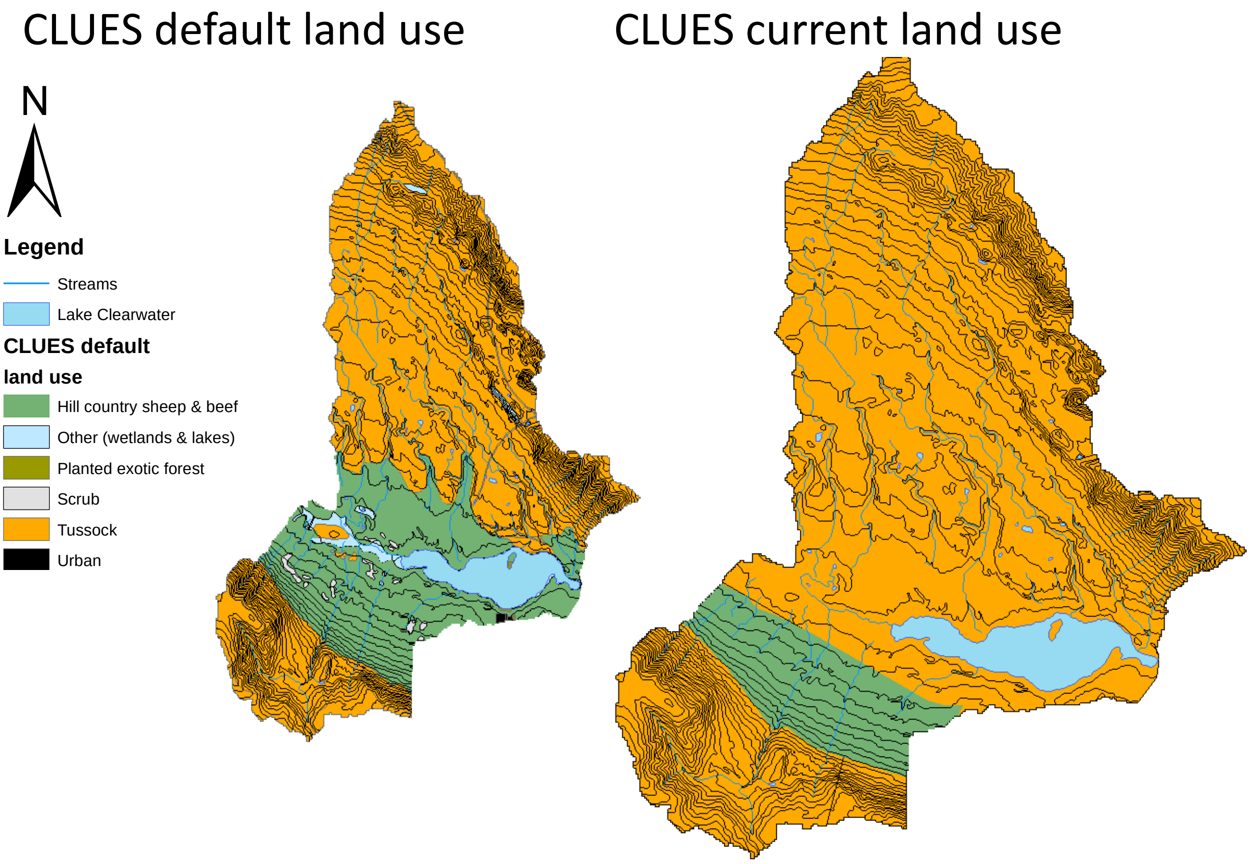

Figure 2-19, Figure showing the two land use scenario used as input for the CLUES model.

2.7.2 Phosphorus source coefficients

The SPARROW model is used to predict TP loads from unfarmed land. Two source coefficients in the SPARROW component of the CLUES model were modified to reduce TP loads in natural catchments. The primary source coefficient for TP load from unfarmed land, labelled as "OtherNonPasture", was adjusted to 0.0012 from the default value of 0.0263 to fit CLUES model predictions to measured TP loads.

Phosphorus is often bound to sediment, so erosion and sediment load can be positively correlated with phosphorus load. As a result, SPARROW predicts additional phosphorus load proportional to predicted sediment load using a second source coefficient. Measured TSS is typically below the detection limit (3 g m^{-3}) in the Lake Clearwater catchment (section 4.2.5). For this reason, the second source coefficient that controls the additional phosphorus load calculated from a sediment loss estimate was set to zero. This sediment loss coefficient did not affect TN load estimates.

3 Hydrology results and discussion

This chapter presents and discusses the results from investigation of the hydrology in the Lake Clearwater catchment. The main aim of the hydrological investigation was to determine runoff processes and annual flows for the calculation of nutrient loads.

3.1 Rainfall

Total annual rainfall at the Hakatere RAWS weather station for 2010-2011 was 606 mm and in 2011-2012 was 605 mm. Total annual rainfall from 2003 until 2012 is shown in Figure 3-4. During winter and spring, lake and wetland water levels were high. Runoff in perennial streams and ephemeral channels was also higher during winter and spring (section 3.5). However, monthly rainfall totals (Figure 3-1 and Figure 3-2) show that rainfall is no higher during winter and spring than in the dry summer-autumn months. Snow and ice melt contribute to higher flows in late winter and spring. High losses from evaporation during warm summer weather may also contribute to lower flow in summer and autumn.

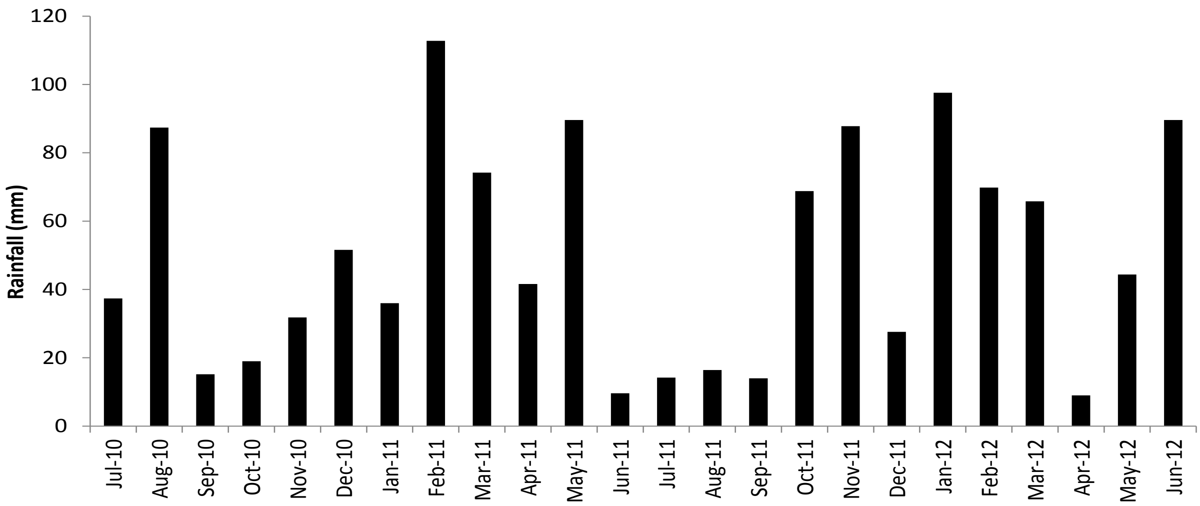

Figure 3-1, Monthly rainfall at Hakatere RAWS from July 2010 to June 2012

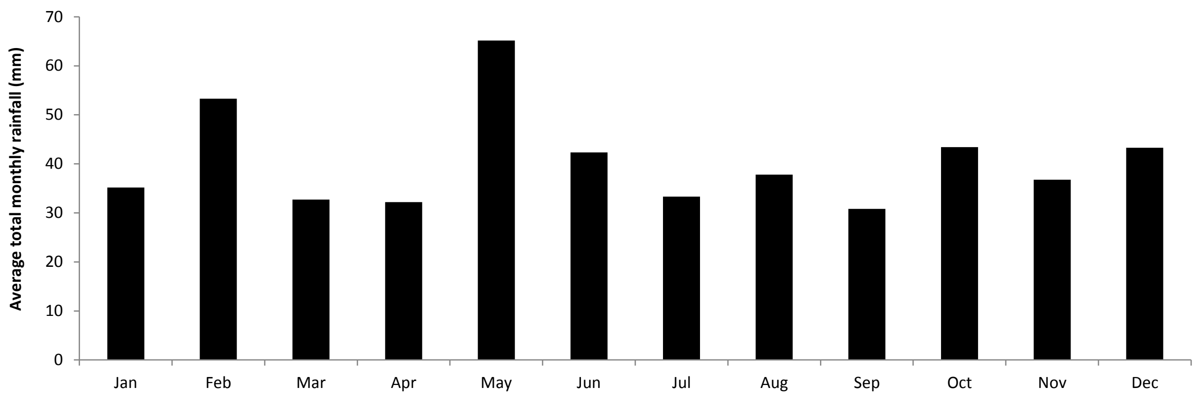

Figure 3-2, Average total monthly rainfall for Hakatere RAWS (2003-2012)

3.2 Evaporation and evapotranspiration

Annual open water and Penman-Monteith potential evapotranspiration (PET) from stations described in section 2.1.2 are shown in Figure 3-3. On average PET estimates from VCN stations (557-665 mm $year^{-1}$) were 78 % lower in the Clearwater catchment than at the Methven CWS (665-865 mm $year^{-1}$). A map of the interpolated mean annual PET total by Tait and Woods (2007) (Figure 1-6) provides a value of 701-800 mm for the Hakatere area and 801-900 mm for the Methven CWS station.

Lake Clearwater is expected to have similar annual evaporation to Lake Tekapo due to the similar climate, latitude, topography and altitude. The main difference between the two lakes is size. This may cause a difference in seasonal evaporation rates because of a difference in thermal mass. Annual evaporation from Lake Tekapo is estimated to be 780 - 990 mm yr^{-1}. The estimated seasonal evaporation rates from Lake Tekapo for spring, summer, autumn and winter are 90, 50, 340 and 300 mm, respectively (Harding et al. 2004). Evaporation from Lake Clearwater could potentially be spread more evenly across the seasons because Lake Clearwater has less thermal mass and therefore requires less sensible heat input in summer to warm the lake and will release less energy for evaporation in autumn and winter.

Loss from the surface of Lake Clearwater due to evaporation was estimated to be $1.34x10^6$ m^3 $year^{-1}$ or 29 mm $year^{-1}$ runoff depth for the Lake Clearwater catchment. This is 5% of total rainfall for the whole catchment, a substantial loss of water from the catchment.

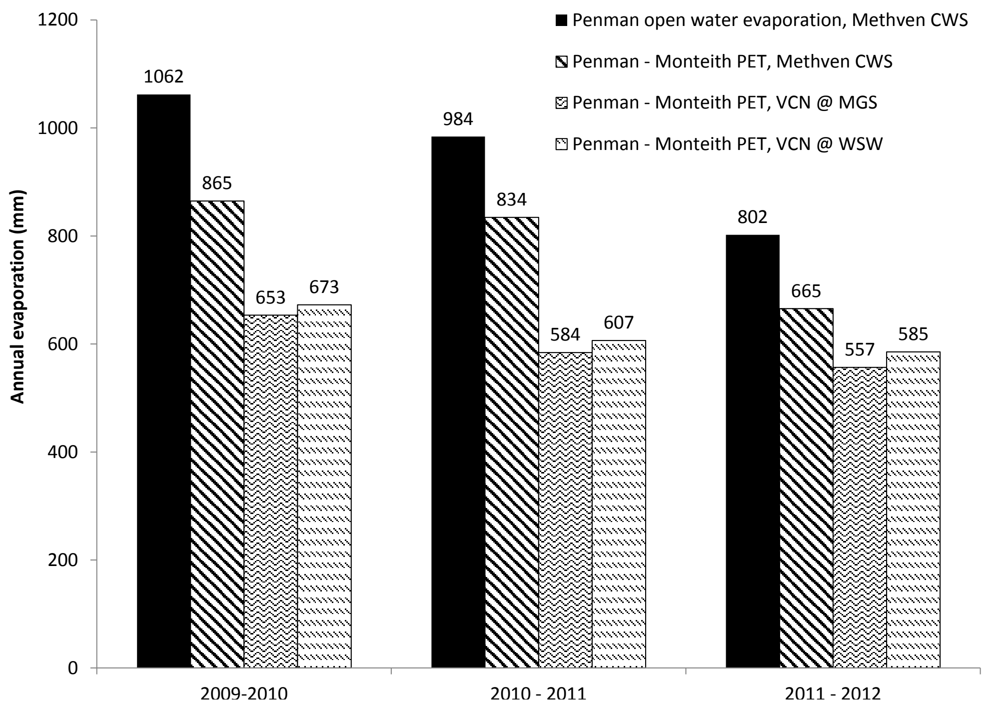

Figure 3-3, Annual evaporation measurements for Methven weather station and estimated PET at two VCN grid points in the Clearwater catchment

3.3 Hakatere rainfall and runoff

Annual rainfall and runoff for the Hakatere basin from 2003-2004 to 2011-2012 is shown in Figure 3-4. Runoff varies to a greater degree than rainfall. Runoff for the catchment above Buicks Bridge is approximately double the runoff from the Hakatere basin.

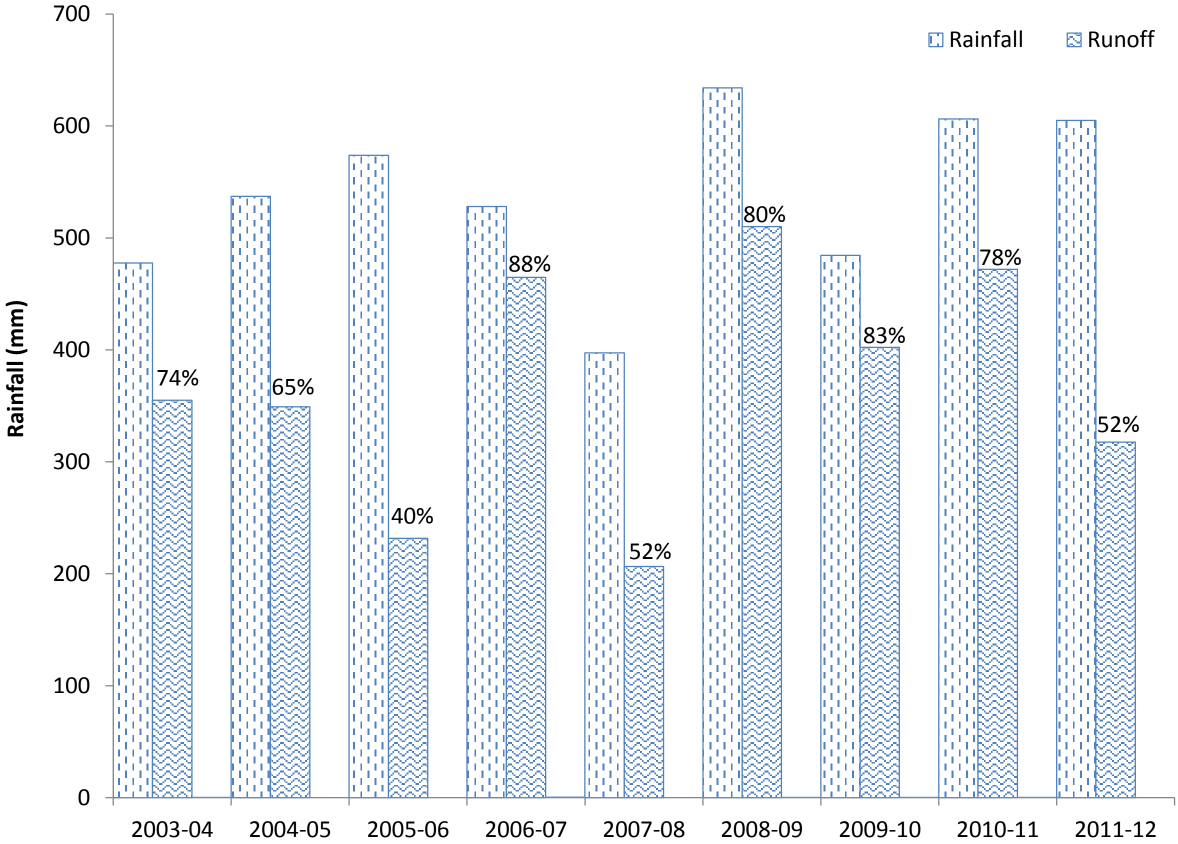

Figure 3-4, Annual rainfall and runoff for the Hakatere area

Average annual values for rainfall and runoff are given in Table 3-1. Values were calculated as the average of annual totals shown in Figure 3-4. Runoff was estimated to be 68% of rainfall in the Hakatere area.

Table 3-1, Average annual values for the Hakatere catchment (South Ashburton River)

Location	mm year^{-1}
Hakatere Rainfall	538
Runoff at Buicks Bridge	1132
Runoff at Mt Somers	577
Hakatere catchment runoff	367
Hakatere catchment loss	171
Runoff as a Percent of rainfall (Average)	68 %

3.4 Surface water flow regimes

Different surface waterways were found to have different flow regimes (Figure 3-6). This is expected due to markedly different catchment topography. Different geology is also expected to affect stream flow generation.

Whisky Stream (WSW) shows rapid response to rainfall (Figure 2-16). Whisky Stream's catchment is steep with a relatively short flow path for runoff to reach the catchment outlet. Flashy flows will likely reduce in stream processing of nutrients in Whisky Stream and may cause erosion. Flow rate versus the probability of exceedance (flow duration curve) for WS3 is shown in Figure 3-5.

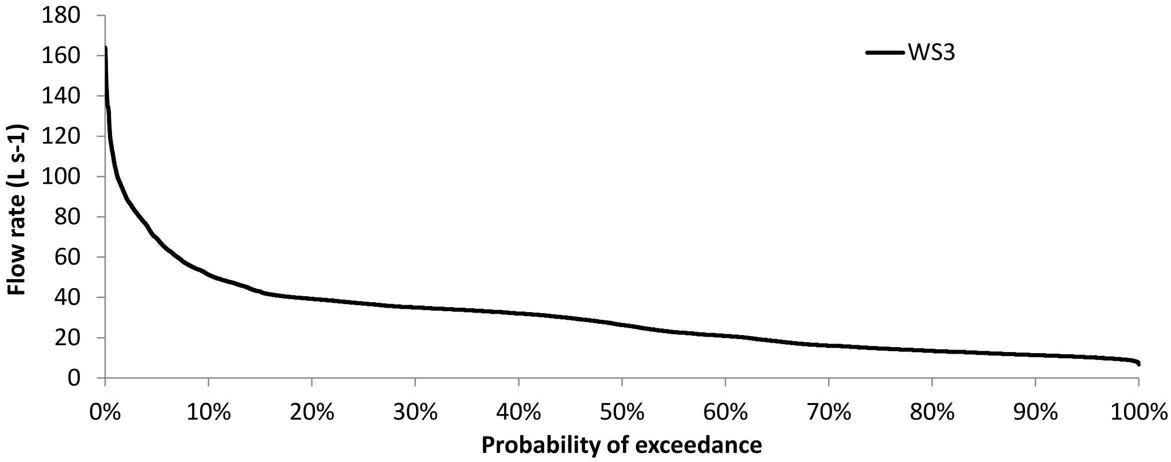

Figure 3-5, Whisky Stream flow duration curve for flow data from July 2011 to June 2012

The flow response for the wetland channel (WC1) is slower. The northern area, approximately 60%, of its catchment, is elongated and less steep (Figure 2-17). This results in a more tortuous flow path for runoff. There is also considerable surface water storage upstream of the wetland channel in the form of shallow wetlands and ponds.

Flow during baseflow conditions at MGS is stable with a very slow recession and MGS shows a delayed response. The reason for this it is not obvious. The MGS catchment is steep and the surface flow path for runoff is short. One explanation for the delayed response is that the dominant stream-flow source is subsurface lateral runoff from the slope to the northeast of Mt Guy Stream channel (Figure 2-17). Subsurface runoff and storage may delay runoff entering Mt Guy Stream and release water slowly as baseflow.

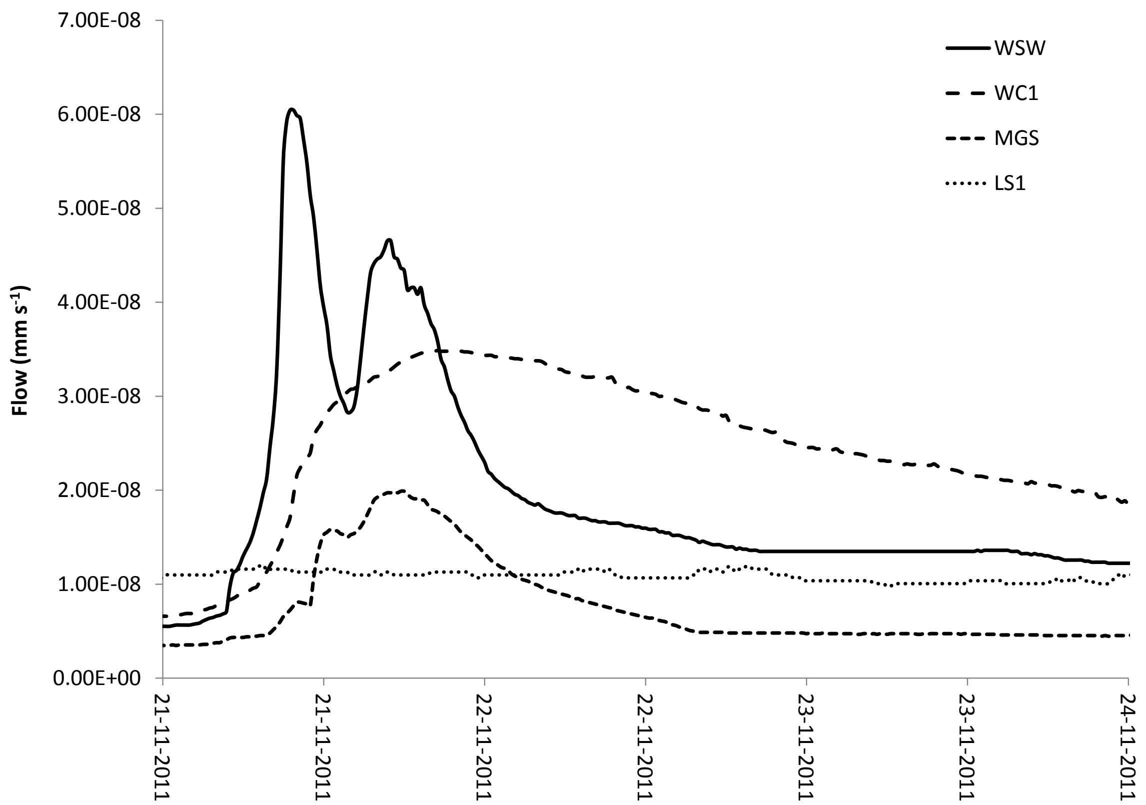

Figure 3-6, Stream flow response to rainfall (21/11/2011)

3.5 Measured annual surface runoff

Annual measured surface water flow is shown in Figure 3-7. The highest surface runoff yield was in Whisky Stream (WS3), 223 mm year^{-1} for 2011-2012. WS3 was expected to provide the most accurate estimate of flow in Whisky Stream. Runoff in the wetland channel was comparable (200 mm year^{-1}).

Ephemeral runoff at RC1, 146 mm year^{-1} for 2011-2012, was inferred from the record at WS3 (section 2.1.4) and is more uncertain than direct measurement. In addition, catchment boundary delineation for RC1 was challenging due to complex terrain and potential subsurface lateral flow sources from surrounding catchments.

Weir flow measurements at MGS estimated runoff at only 100 mm year^{-1} in 2011-2012. This could be due to considerable subsurface flow out of the catchment. However, this was not investigated.

LS1 is also lower than expected with 88 mm year^{-1} of runoff for 2011-2012. Lambies Stream is the only surface outlet to Lake Clearwater. Low surface flow from the lake could be due to very high evaporation from the lake or subsurface outflow from the lake. Evaporation from the lake surface was estimated to be 29mm year^{-1} (section 3.2) and subsurface flow out of the lake could also potentially be large.

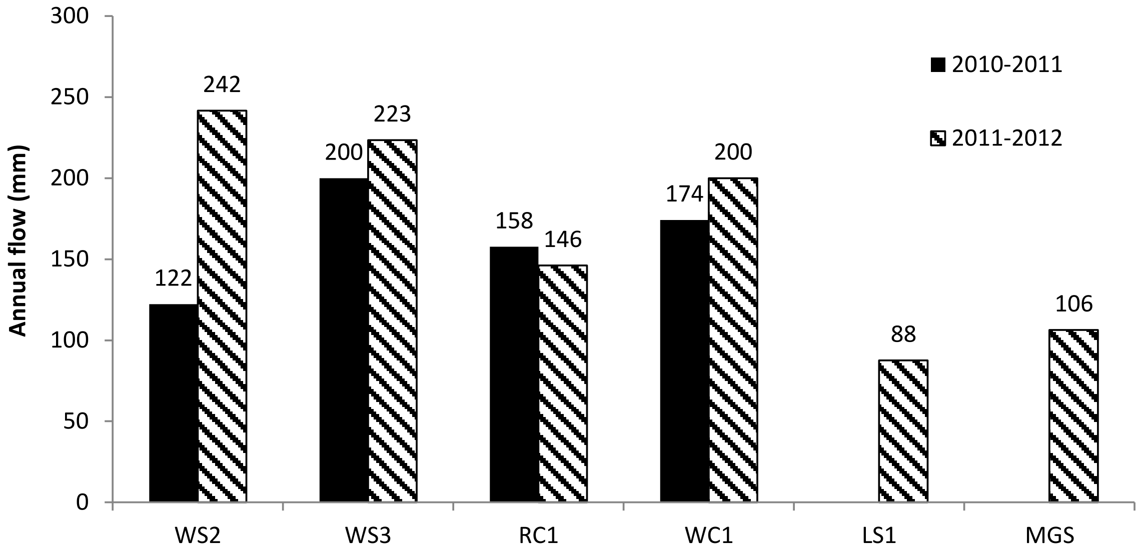

Figure 3-7, Annual measured surface runoff

Flow rate in streams varies with season; during 2010, 2011 and 2012 flow rate in summer and autumn was, on average, only 27 % of flow rate in winter and spring. Table 3-2 shows the average flow rate at WC1 for each season.

Table 3-2, Average monthly flow rate and volume at WC1 from 2010 until 2012

Season	Average flow rate at WC1 (l s^{-1})	Runoff (mm)	Runoff (%)
Summer	37	11	8
Autumn	45	17	13
Winter	142	58	42
Spring	167	51	37

3.6 Comparison of weir and stream rating-curve flow estimation

A hydrograph for Whisky Stream during a storm event on the 21st of November 2011 is shown in Figure 3-8. The weir (WSW) is expected to be accurate to within 5% (Murray and Ackroyd 1979). WS2 flow measurements over predict flow initially during preceding baseflow conditions and under predict flows after the high flow event. In addition, observations before and after this high flow event showed that vegetation and debris was washed from the channel at WS2. It is likely that after high flow rates the channel was altered and the relationship between stage and discharge changed. The changeability of the channel conditions at WS2 may introduce error into flow measurement at this site. WS2 gave unexpectedly large differences in flow between 2010-2011 and 2011-2012, whereas WS3 shows little difference between years. WS3 showed a lower peak flow than WSW and WS2, which might be due to the small channel at WS3 being over topped in very high flows.

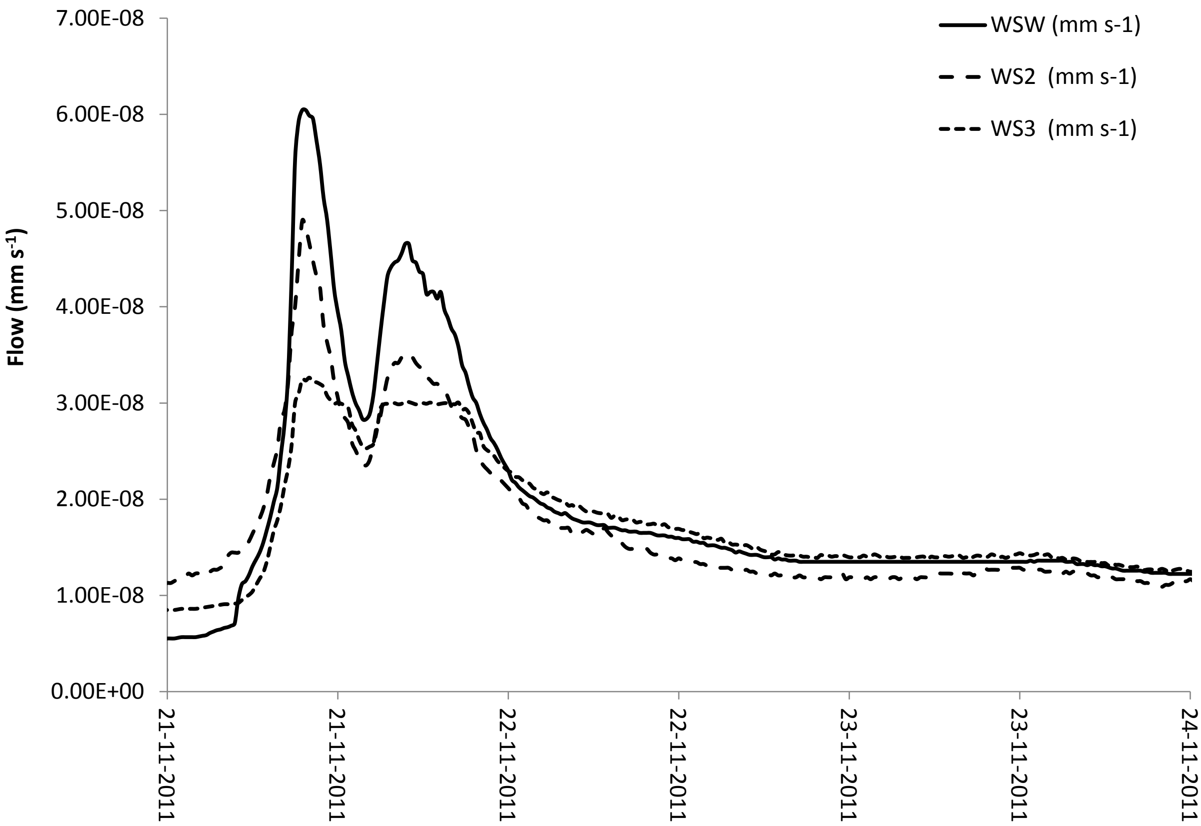

Figure 3-8, Whisky Stream hydrograph from 21st to 24th of November 2011

3.7 Subsurface runoff from the farmed hillslope

Estimation methods for subsurface runoff from the farmed hillslope had considerable uncertainty. To increase confidence in results several methods were used and the results compared (Table 3-3). Each method produced a similar value and this increased confidence in the results. Darcy's equation estimates are shown as values calculated from the low, middle and high estimates of saturated hydraulic conductivity.

Table 3-3, Estimations of subsurface runoff yield from the farmed hill slope

Estimation Method	Subsurface runoff
Water balance	136 mm $year^{-1}$
TN nutrient mass balance	79-149 mm $year^{-1}$
TP nutrient mass balance	81-136 mm $year^{-1}$
Darcy's equation (low-mid-high)	1.25-127-12692 mm $year^{-1}$

For the water balance method, the total runoff depth from the farmed hill slope was assumed to be the same as total annual runoff depth calculated for the Hakatere catchment (Section3.3). If total runoff from the farmed hillslope is less than that of the Hakatere catchment, subsurface runoff using this method will be an overestimate. Subsurface runoff estimates using Darcy's equation are also subject to considerable uncertainty. Many assumptions are made about the subsurface geology (section 0). In addition, estimates of saturated hydraulic conductivity of the subsurface geology vary over four orders of magnitude.

Total subsurface nutrient load from the farmed hillslope was assumed to be the residual load from TN and TP nutrient balances around the wetland channel (section 2.6.2). The total annual subsurface nutrient load was used to calculate the total annual subsurface runoff volume. There are several important sources of uncertainty from this method. The farmland is assumed to be the only significant source of nitrogen loading into the wetland channel. If subsurface nutrient load from any other source were significant, the runoff estimate from this method would be an overestimate. The surface water wetland channel is assumed to be the only important flow out of the wetland. If significant flow and nutrient load exits the wetland as subsurface flow, the subsurface runoff estimate from this method will be an underestimate. Finally the measurement uncertainty for the total ephemeral load from the farmed land is considerable. If the ephemeral load is under or overestimated, the estimate from this method will over or underestimate subsurface runoff, respectively.

Although there is considerable uncertainty in estimates of subsurface results, all results suggest that subsurface runoff is significant and is an important transport pathway for nutrients into the Lake Clearwater wetland. This study gives a range of subsurface runoff into the wetland of 79-146 mm $year^{-1}$ with a median value of roughly 136 mm $year^{-1}$. This represents 38% of total runoff from the farmed hillslope.

3.8 WATYield model results

The modified WATYield model was first run with input parameters set to the most appropriate values, from literature, for the Whisky Stream catchment (4.51 km^2). This resulted in a large over prediction of runoff. The model was calibrated to give the best possible fit to Whisky Stream flow data (2010-2012). Reasonable fit was achieved but flow predictions during wetter periods (winter and spring) had large errors. Once fitted as well as was possible to the flow record at Whisky Stream, the model was run for new flow data at Whisky Stream and predictions of flow failed to validate the model's ability to predict temporal flow patterns in Whisky Stream. Temporal flow pattern predictions were improved by using a fixed daily PET estimate instead of Whisky Stream VCN station PET data. However, this is not realistic as measured PET is shown to vary daily with weather conditions and seasonally (Harding et al. 2004).

Due to temporally variable performance and large uncertainty, the model was not considered reliable enough to provide estimates for runoff or actual PET in the Lake Clearwater catchment. It is thought the modelled processes are too simplistic to represent temporal patterns in flow sufficiently for the small Whisky Stream catchment. In addition, the model does not consider shallow subsurface runoff bypassing Whisky Stream and flowing directly into the wetland channel at the valley floor. Estimates of subsurface flow (section 3.7) suggest that subsurface runoff represents a considerable portion of total runoff from the Whisky Stream catchment.

4 Water quality results and discussion

This section presents the results from laboratory sample analysis and *in-situ* measurements for waterways in the catchment.

4.1 Statistical analysis results

Water quality data were analysed to identify correlation between parameters and significant differences between sites and waterways. Analysis was carried out using the spread sheet-based software XLStat (XLSTAT 2012). Non-detects were removed from the data set to avoid obtaining statistically significant differences between sites based on values predicted by ROS.

4.1.1 Correlation between sample analytes

Pearson correlation between each sampling parameter was evaluated. This analysis was helpful for highlighting any relationships between the parameters that might be of interest. Inspection of scatterplots for each combination of parameters also gave insight into the relationships between parameters. Table 4-1 shows a correlation matrix that identifies linear correlation between two parameters. Further correlation test results, including p-values, scatterplots and coefficients of determination (R^2) can be found in Appendix E.

TSS, NH_4 and TP are shown to be positively correlated indicating that these analytes may share a source. It is expected that the related processes of direct input, overland flow, and erosion are the primary source for these analytes. These processes will occur most commonly during periods of high rainfall intensity. NH_4 and NO_3^- also show a correlation. However, this correlation results from a single sample of subsurface flow in which NH_4 was abnormally high so should be treated with caution. TN and TKN are highly correlated. This is expected, as TKN comprises most of the TN in surface water. SC was strongly correlated with DRP. This indicates that DRP is a dominant ion in samples with elevated SC.

Table 4-1, Correlation matrix (Pearson) for sampling parameters, Values in bold have a P value <0.05 (Redder colours indicates a strong positive correlation and colours towards green indicate a negative correlation value)

Variables	TSS	TN	NH_4	NO_3^-	TKN	DRP	TP	pH	DO	Temp	SC
TSS	**1**										
TN	0.324	**1**									
NH_4	**0.758**	0.504	**1**								
NO_3^-	**0.524**	**0.303**	**0.938**	**1**							
TKN	0.168	**0.976**	0.339	0.229	**1**						
DRP	0.391	**0.585**	-0.277	0.157	**0.709**	**1**					
TP	**0.568**	**0.623**	**0.834**	**0.586**	**0.492**	0.350	**1**				
pH	-0.413	**-0.386**	-0.537	**-0.476**	**-0.357**	-0.082	**-0.267**	**1**			
DO	0.102	0.083	0.460	**-0.402**	0.180	0.382	0.182	0.227	**1**		
Temp	-0.110	-0.039	-0.261	0.092	-0.071	**-0.673**	-0.036	-0.077	**-0.642**	**1**	
SC	0.041	0.044	-0.298	0.141	0.118	**0.742**	-0.111	**-0.289**	-0.159	0.096	**1**

4.1.2 Non-parametric testing

Non-parametric testing was used to investigate whether grouping of sites into the same waterway was appropriate for the calculation of nutrient loads. Two non-parametric one-way analysis of variance methods were used because they assume no homogeneity or normal distribution. The non-parametric Kruskal-Wallis test was applied to TN and TP concentrations at each site. The test found that at least one site had significantly different concentration values (Appendix G). Pairwise comparisons of TN and TP concentrations between sites were made using the Dwass-Steel-Critchlow-Fligner method. The P-value was evaluated for pairwise comparisons of nutrient concentrations between each site (Table 4-2 and Table 4-3). The hypothesis of non-difference between sites can be rejected to the accepted level of significance (5%) when the p-value is below 0.05.

Table 4-2, Table showing P-values (values in bold indicate a p-value below 0.05) for pairwise comparisons of TN concentrations between all sites using the non-parametric Dwass-Steel-Critchlow-Fligner method (redder colours indicate highly significant difference and colours towards green indicate no significant difference)

	WS1	WS2	WS3	RC1	RC2	RC3	S1	S4	S5	USW	WC1	WC2	WC3	LS1	MGS
WS1	**1**														
WS2	1.000	**1**													
WS3	1.000	1.000	**1**												
RC1	0.219	0.129	0.182	**1**											
RC2	0.509	0.412	0.473	0.899	**1**										
RC3	0.509	0.412	0.546	1.000	1.000	**1**									
S1	0.217	0.129	0.180	0.804	0.991	1.000	**1**								
S4	0.757	0.699	0.816	0.835	0.924	1.000	0.966	**1**							
S5	0.757	0.699	0.738	0.835	0.924	1.000	0.998	0.997	**1**						
USW	1.000	1.000	1.000	0.638	0.820	0.820	0.628	0.924	0.924	**1**					
WC1	0.958	0.944	0.954	0.224	0.520	0.931	0.989	1.000	1.000	0.996	**1**				
WC2	0.980	0.850	0.937	0.362	0.834	0.950	0.965	1.000	1.000	0.992	1.000	**1**			
WC3	0.882	0.723	0.771	0.834	0.999	0.999	1.000	1.000	1.000	0.972	1.000	0.997	**1**		
LS1	0.077	**0.029**	0.054	1.000	1.000	1.000	0.956	0.738	0.738	0.473	0.258	0.344	0.829	**1**	
MGS	1.000	1.000	1.000	0.638	0.820	0.820	0.628	0.924	0.924	1.000	0.990	0.736	0.820	0.473	**1**

This test shows that differences in TN between most sites were not significant enough to reject the possibility of no difference between sites (P<0.05). Although significant differences between sites are not shown, the sample sizes were small for this type of test and p-values would be likely to decrease with more samples. Sites with even fewer samples such as the seeps might not give a reliable result. A significant difference between WS2 and LS1 was indicated; both sites have a large number of samples and show a considerable difference in concentration. No significant differences in TP concentration between sites were found (Table 4-3). TP concentrations are seen to be much more variable throughout the catchment. Large p-values suggest that the likelihood of significant difference in TP concentration between sites on the same waterway is very low. The lack of significant difference between sites in the same waterway indicates that grouping of sites into Whisky Stream sites, ephemeral culvert sites, and subsurface lateral flow sites for calculation of TN and TP loading is appropriate.

Table 4-3, Table showing P-values (values in bold indicate a p-value below 0.05) for pairwise comparisons of TP concentrations between all sites using the non-parametric Dwass-Steel-Critchlow-Fligner method (redder colours indicate highly significant difference and colours towards green indicate no significant difference)

	WS1	WS2	WS3	RC1	RC2	RC3	S1	S4	S5	USW	WC1	WC2	WC3	LS1	MGS
WS1	**1**														
WS2	1.000	**1**													
WS3	1.000	1.000	**1**												
RC1	0.425	0.222	0.484	**1**											
RC2	0.831	0.831	0.979	0.992	**1**										
RC3	0.685	0.685	0.834	1.000	1.000	**1**									
S1	0.929	0.831	0.998	0.736	0.999	1.000	**1**								
S4	1.000	1.000	1.000	0.835	0.924	0.998	1.000	**1**							
S5	0.992	0.998	1.000	0.835	0.924	0.998	0.979	1.000	**1**						
USW	0.912	0.954	0.993	1.000	1.000	0.998	1.000	1.000	1.000	**1**					
WC1	0.943	0.942	1.000	0.604	1.000	0.958	1.000	1.000	1.000	1.000	**1**				
WC2	0.919	0.918	1.000	0.180	0.469	0.947	0.818	1.000	1.000	1.000	1.000	**1**			
WC3	0.929	0.958	1.000	0.638	0.820	0.999	0.999	1.000	1.000	1.000	1.000	1.000	**1**		
LS1	0.816	0.811	1.000	0.182	0.949	0.951	0.999	1.000	1.000	1.000	1.000	1.000	1.000	**1**	
MGS	1.000	1.000	0.979	0.219	0.509	0.590	0.509	1.000	0.977	0.910	0.722	0.568	0.681	0.402	**1**

To evaluate differences between waterways, samples from each site were grouped together according to which waterway the sample was taken from. With a larger sample size, it was possible to reject the non-difference hypothesis for several sites (Table 4-4).

Table 4-4, Table showing P-values (values in bold indicate a p-value below 0.05) for pairwise comparisons of TN concentrations between waterways in the Lake Clearwater catchment using the non-parametric Dwass-Steel-Critchlow-Fligner method (redder colours indicate highly significant difference and colours towards green indicate no significant difference)

	Whisky Stream	Culverts	Seeps	USW	Wetland	Lake	MGS
Whisky Stream	**1**						
Culverts	**< 0.0001**	**1**					
Seeps	**0**	0.108	**1**				
USW	1	0.135	0.157	**1**			
Wetland	**0.034**	**0.004**	0.816	0.681	**1**		
Lake	**0.001**	1	0.125	0.176	**0.015**	**1**	
MGS	1	0.135	0.157	1	0.366	0.176	**1**

By grouping the samples into waterways, it was possible to reject the non-difference hypothesis for TP concentration between Whisky Stream and the culvert sites, the seeps, Lambies Stream and the main wetland channel (Table 4-5). USW and the seeps sites were not significantly different from the other sites using this test. However, this was probably primarily due to the low number of samples taken for these sites.

Table 4-5, Table showing P-values (values in bold indicate a p-value below 0.05) for pairwise comparisons of TP concentrations between waterways in the Lake Clearwater catchment using the non-parametric Dwass-Steel-Critchlow-Fligner method (redder colours indicate highly significant difference and colours towards green indicate no significant difference)

	Whisky Stream	Culverts	Seeps	USW	Wetland	Lake	MGS
Whisky Stream	**1**						
Culverts	**0.002**	**1**					
Seeps	0.7	0.073	**1**				
USW	0.578	0.986	0.997	**1**			
Wetland	0.168	**0.006**	0.999	0.996	**1**		
Lake	0.364	**0.046**	1	1	1	**1**	
MGS	0.883	**0.01**	0.203	0.567	0.076	0.141	**1**

4.1.3 Principal component analysis (PCA)

A PCA analysis was used to evaluate the similarities between sites in the same type of waterways taking into account all sampling parameters. Median values for ten measured analytes at each site were used for the analysis. Figure 4-1 plots each site in terms of two principal components (F1 & F2) that explain 65.3% of variability in the samples.

Grouping of sites into similar types of waterways can be seen in this plot. The groundwater seeps are clearly dissimilar to the other sampling sites. This is expected as subsurface flow is subject to very different conditions compared with surface water. Small fast flowing streams (WS1-3, USW & MGS) are grouped to the left. Although Whisky Stream is impacted by farmland, it still has many characteristics in common with the un-impacted Mount Guy Stream (MGS) and upstream wetland (USW). The sites in the main wetland channel (WC1-3) are all grouped together. This is expected as the sites are all along the same channel. The lake outlet (LS1) and the road culverts (RC1-3) are all spread to the right of the graph, most likely due to higher nutrient concentrations.

Although the similarities between sites can be seen from direct examination of the data, PCA analysis was useful to check if grouping of sites for calculation of nutrient loads is valid. This analysis suggests that grouping of Whisky Stream sites (WS1-3), groundwater seep sites (S1-5) and wetland channel sites (WC1-3) is a valid approach.

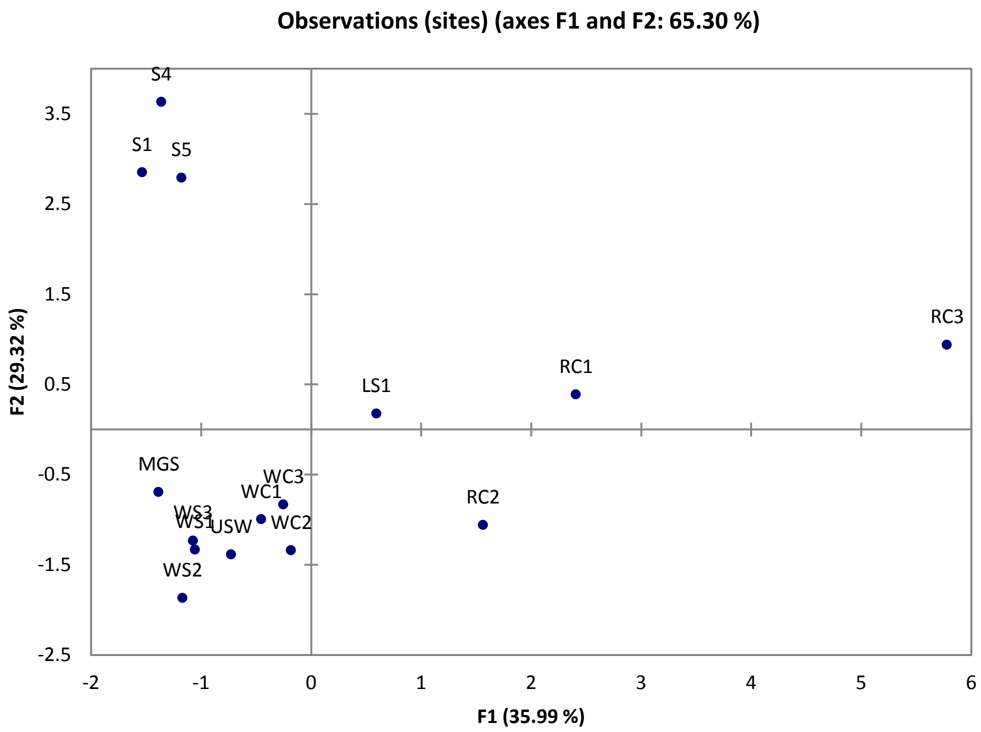

Figure 4-1, Plot of sites with respect to principal components F1 & F2

4.1.4 Summary of statistical analysis

Non-parametric testing indicated nutrient concentrations between sites in the same waterway were not significantly different, but some significant differences between waterways existed. PCA analysis also showed distinct grouping of sites in the same waterway and waterway type. Therefore, grouping of sites to calculate one nutrient load for each waterway was appropriate. Statistical testing was useful to evaluate if significant differences occur in each waterway. Table 4-6 shows waterway-specific findings from analyses.

Table 4-6, Summary of findings from statistical analysis of differences in nutrient concentrations between sites

Whisky Stream	• Whisky Stream TN concentrations were significantly lower than all other waterways in the catchment apart from those draining natural catchments (USW and MGS).
Road culverts	• The TN concentrations in road culvert sites were significantly different from Whisky Stream and the wetland channel • The TP concentrations in road culvert sites were significantly different from Whisky Stream, MGS, the wetland channel and the lake outlet
Seeps	• The seeps were not significantly different in TN or TP concentration to the wetland channel or culvert sites; however, when all parameters are considered in PCA analysis the water signature was shown to be clearly different.
Upstream wetland	• Significant differences between the USW site and other waterways could not be seen; however, this was likely due to the small number of samples at this site.
Main wetland	• Nutrients were significantly lower in the wetland channel than the culvert sites
Mount Guy Stream	• Significant differences between Mount Guy Stream and other waterways were not present due to the small sample size
Lambies Stream	• Lambies Stream was significantly higher in TN than Whisky Stream • Lambies Stream, the outlet of the lake, was significantly higher in TN than the wetland channel which forms the major inlet to Lake Clearwater

4.2 Water quality indicators

Dissolved oxygen, pH, temperature and specific conductance were measured to highlight water quality differences between waterways. The results are presented in the following sections. All box plots show the median as red line. The box represents the range from the 25th to 75th percentiles, and the whiskers extend to the most extreme values.

4.2.1 pH

pH measured *in-situ* ranged between 5.9 and 8.1 and was generally close to pH 7, which is typical for New Zealand rivers (Harding et al. 2004). pH measurements across all sites are shown in Figure 4-2. pH varied up to 20% between sampling events. For example, pH varied between 6.6 and 8.2 S.U. in Whisky Stream. pH was consistently lower in the ephemeral channels (RC1 and RC2) and the seeps (S1-3). pH in the stormflow composite sample (7.9 S.U.) was close to the median value of pH in all samples in Whisky Stream. This indicates significant changes in pH do not occur during storms.

pH is higher than typical values (4.9-6 S.U.) for rainfall in New Zealand (Halstead et al. 2000). Higher pH in waterways typically results from buffering by bicarbonate (Harding et al. 2004). pH is also likely to be higher in surface water than in wetlands as contact with soil may lower pH in water flowing through the wetland. Clarkson *et al* (2003, as cited in Harding et al. 2004) provide a range of soil pH of 3.4-4.4 S.U. for New Zealand bogs and 4.1-5.9 S.U. for swamps.

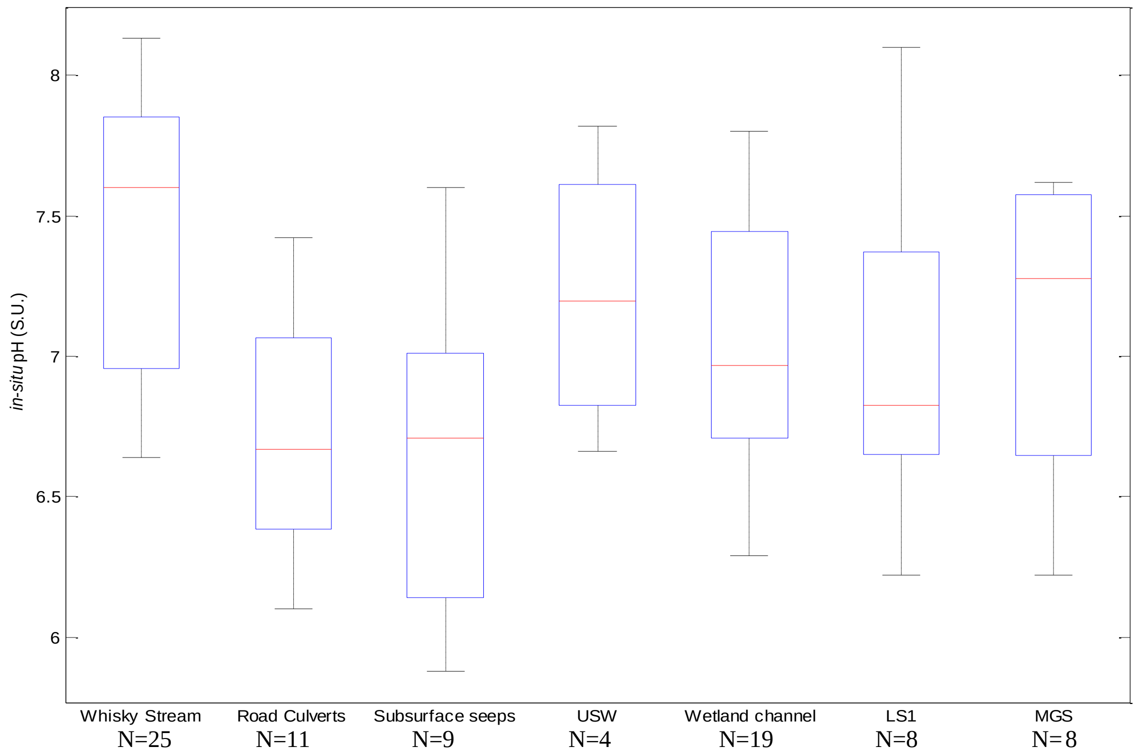

Figure 4-2, Boxplots of pH sampled *in-situ*

4.2.2 Dissolved oxygen (DO)

DO measurements show that the surface waters (WS1-3, RC1-2, WC1-2, USW, LS1 and MGS) of the catchment are saturated with oxygen (Figure 4-3). DO concentrations ranged between 8.6 and 13.9 g m^{-3}. Dissolved oxygen during the automatic stormflow sampling event was very close to 100% saturation (11.3 g m^{-3}) as would be expected in turbulent high flow events. DO was higher in winter because the solubility of oxygen is greater in colder water than in warm water (APHA 1992). Other factors affecting DO in surface water may be stream turbulence and/or photosynthesis by aquatic plants (Harding et al. 2004). DO is consistently lower in subsurface water seeps. This is expected as subsurface water has less opportunity to equilibrate with atmospheric oxygen and consequentially has lower DO (Freeze and Cherry 1979).

The National Institute of Water and Atmospheric Research (NIWA) states that waters containing above 6 g m^{-3} of DO are safe for the protection of aquatic life (NIWA, 2010). The ANZECC guidelines for DO in upland rivers provide a range of 99-103% saturation (9.9 – 10.3 g m^{-3} at 15°C). However, this guideline is of limited use due to seasonal and diurnal variation (ANZECC 2000).

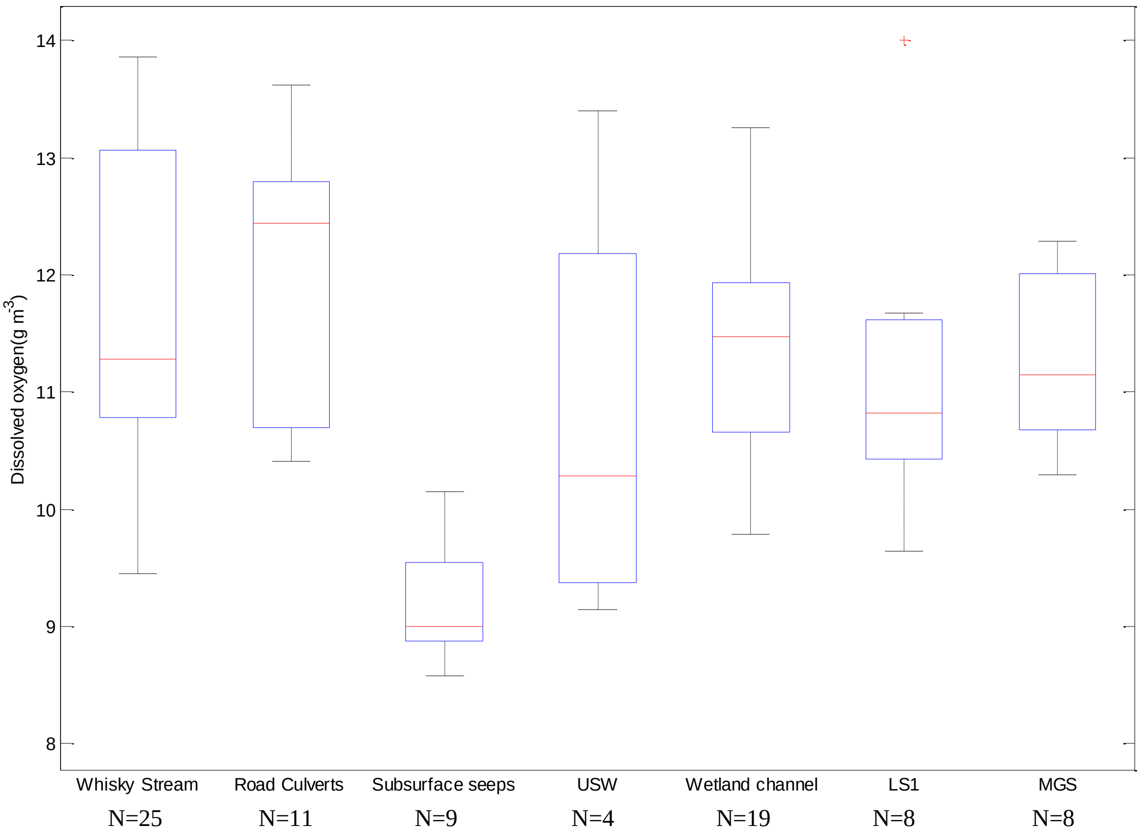

Figure 4-3, Boxplots of dissolved oxygen sampled *in-situ*

4.2.3 Temperature

Temperature measured *in-situ* at each sampling event is shown in Figure 4-4. Variation in temperature between surface waterways for each sampling event is affected by time of day and the thermal mass of the waterway being measured. Temperature is plotted as a scatter plot of temperature at each sampling event versus time of year to show temporal trends.

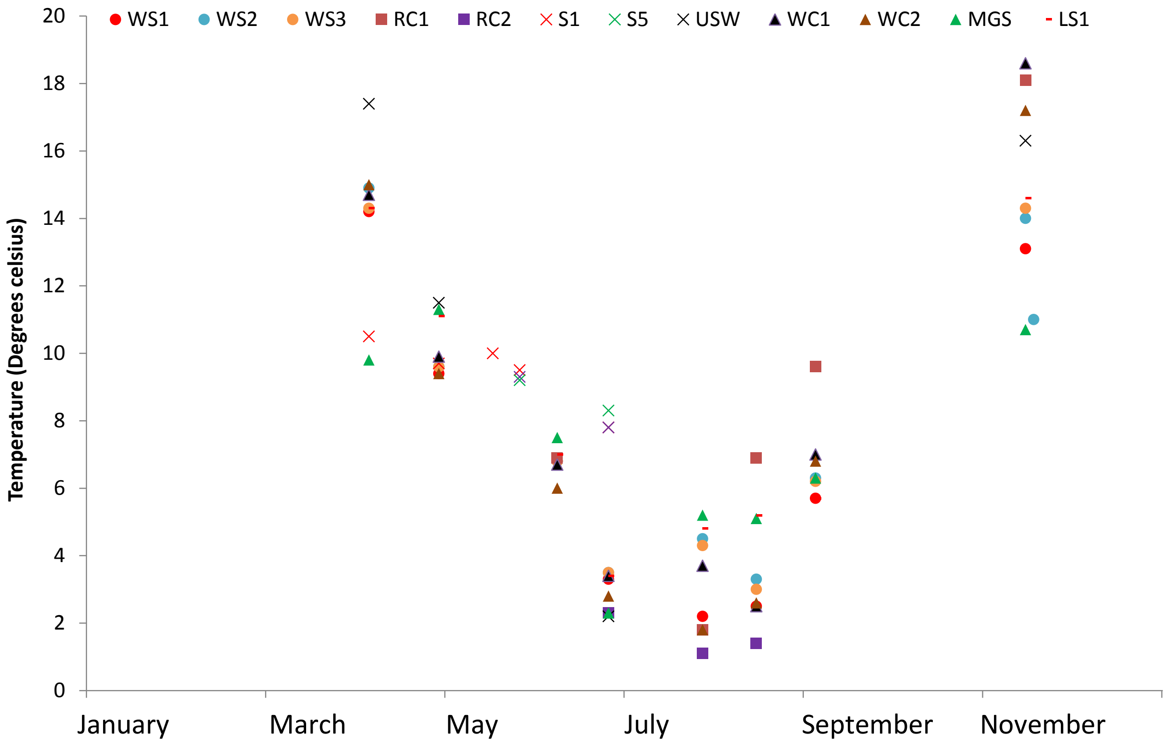

Figure 4-4, Temperature measured *in-situ* across all sites for each sampling event.

The subsurface seeps (S1 and S5) typically showed different temperatures to the surface water for the same sampling event. Subsurface water temperature cooled from 10°C to 7°C from April to August while surface water dropped from 14°C to 3°C. Water temperature at the seep sites was lower in summer and higher in winter relative to surface water. Subsurface water temperature fluctuations were gradual throughout the year due to insulation and thermal mass, whereas surface water temperatures vary strongly on a daily and seasonal basis (Kalbus et al. 2006). The seasonal difference in temperature between surface and groundwater likely indicated that water flowing from the seeps comes from a subsurface lateral flow source rather than a nearby surface water source.

4.2.4 Specific conductance (SC)

SC measured *In-situ* (temperature adjusted) for each sampling event at each site is shown in Figure 4-5. SC ranged between 13 and 73 µs cm^{-1}. SC was generally below the median value for hill-fed upland streams in Canterbury (80 µs cm^{-1}) but agrees well with median values for Canterbury rivers in their natural state (40 µs cm^{-1}) and Canterbury alpine fed upland rivers (60 µs cm^{-1}) (Stevenson et al. 2010). USW showed lower values of specific conductance (median 20 µs cm^{-1}) compared to other sites. This could be due to the small sample size not capturing seasonal variation in SC. This could also be due to low dissolved nutrient concentration, as all samples at USW had low concentrations of dissolved inorganic nutrients. The seeps had the highest median SC concentration and were also relatively high in NNN and DRP.

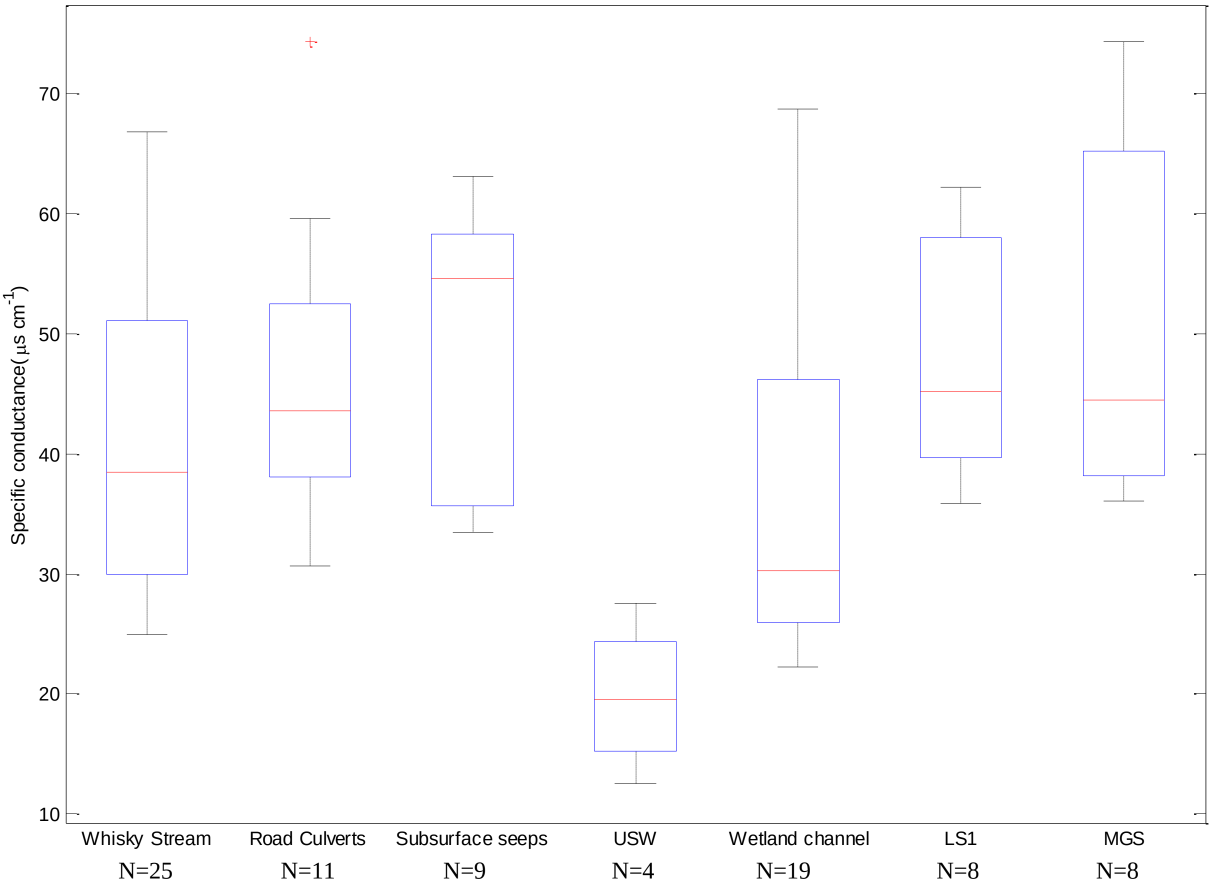

Figure 4-5, Boxplots of specific conductance from *in-situ* sampling

SC was elevated during the first flush of a storm and then returned to normal levels during the recession limb of the storm hydrograph (Figure 4-6). This indicates that dissolved solids, such as dissolved forms of nutrients, are elevated during the first flush of storms. SC is an indirect measure of the concentration of total dissolved solids and the presence of dissolved nutrients can influence specific conductance readings. SC and DRP were positively correlated with a R^2 value of 0.55 (Appendix E). This was the only significant ($p<0.05$) correlation between SC and a nutrient analyte. This suggests that the elevated SC at the beginning of the storm could be due to a first flush of DRP in the rising limb of the flow event.

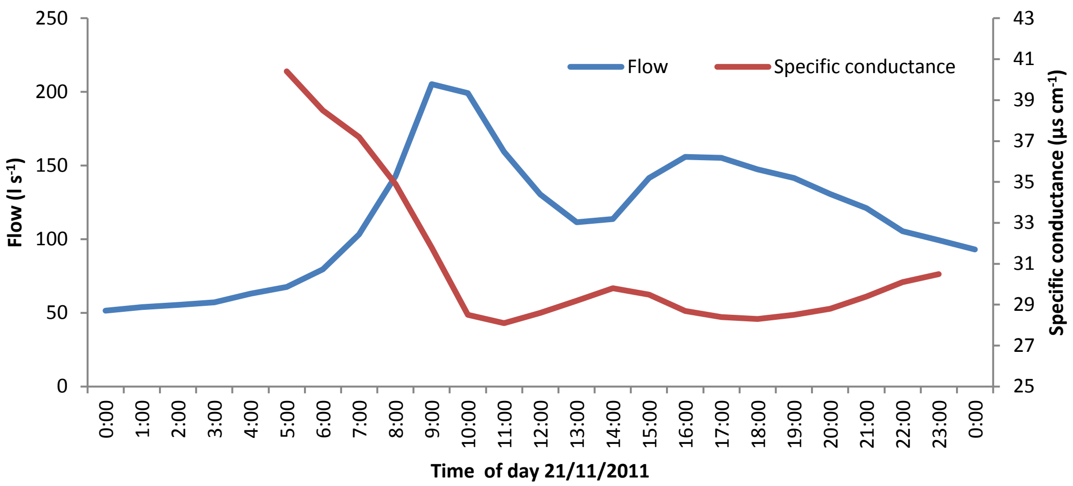

Figure 4-6, Whisky Stream hydrograph and specific conductance for November 21st 2011

4.2.5 Total suspended solids (TSS)

Total suspended solids (TSS) concentrations are shown in Figure 4-7. Data are not shown as boxplots because sample size at each site was not sufficient. This was because TSS concentration in a large proportion of samples was below the detection limit of 3 g m^{-3}.

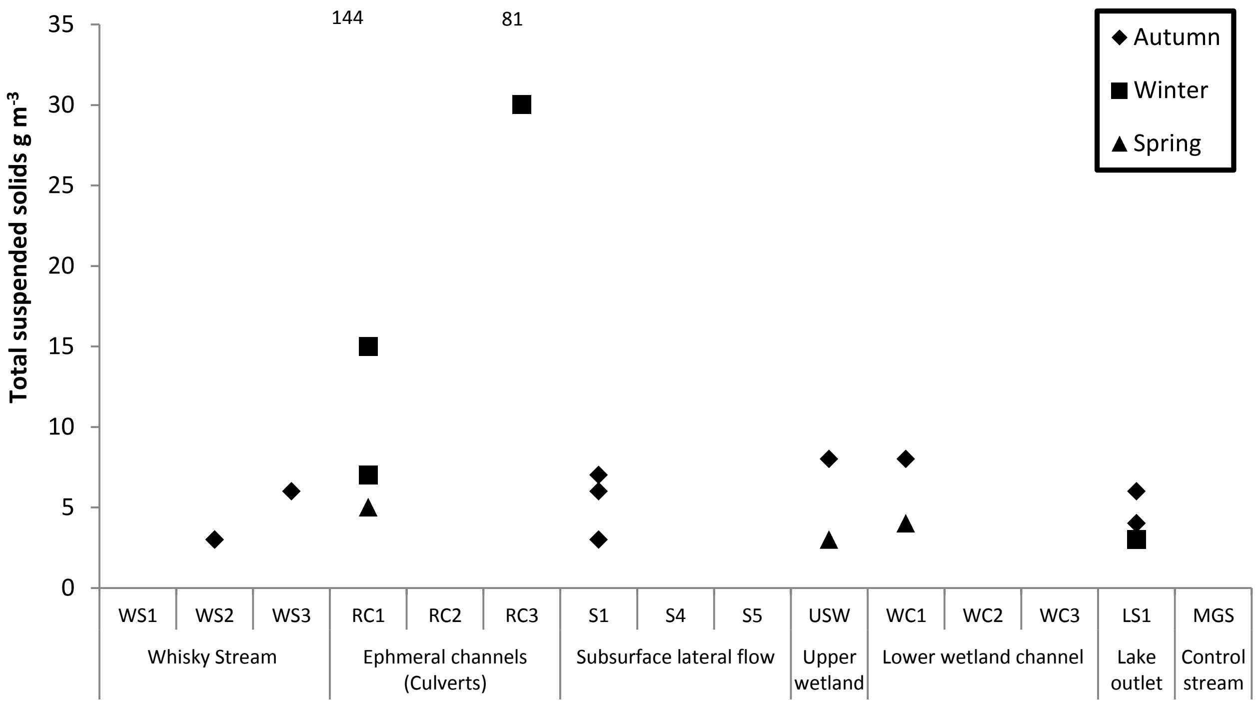

Figure 4-7, Total suspended solids concentration across all sites for all sampling events

TSS concentration was below the detection limit for 87% of samples at all sites. The ephemeral channels (RC1-3) were the exception. TSS was commonly elevated in the ephemeral channels draining farmland. Erosion from sheep and cattle access to the channel is a potential cause of suspended sediment. The channels are used as a drinking water source and pugging of the soft muddy soil in the channel is evident. Erosion from pugging and defecation from livestock could elevate TSS. Dust and erosion from the gravel road directly over the culvert sampling sites is also a potential source of sediment. Water in ephemeral channels directly upstream was observed to have reduced clarity when visually compared to elsewhere in the catchment. A threshold value of 25 g m^{-3} TSS for the onset of detrimental effects due to sediment suspension and deposition is stipulated (Stevenson et al. 2010). Sediment concentration in the ephemeral channels did not often exceed this value and small resultant loadings are not expected to be of concern for water quality in the catchment. TSS was observed to settle downstream in the ephemeral channels or wetland.

TSS concentration was below the detection limit in the stormflow composite sample. This indicates that erosion of sediment during high flows is not of concern in Whisky Stream. TSS concentration is expected to be higher in the first flush of runoff than the composite result, since suspended solids were visibly evident in the first two samples.

Concentrations of TSS found at monitoring sites, other than the ephemeral culverts, are believed to be due to natural erosion processes. Values in this study fall within expected values (0-5 g m^{-3}) for hill-fed upland streams in Canterbury (Stevenson et al. 2010), which are low and unlikely to cause concern for waterways in the Lake Clearwater catchment.

4.3 Nutrients

Water samples were analysed for nutrient concentration to assess water quality and provide median concentrations for calculation of loads and yields. The results are presented in the following sections.

4.3.1 Total nitrogen (TN)

TN concentrations in waterways for all sampling events are summarized in Figure 4-8. The ANZECC trigger value for TN in upland rivers in New Zealand with slightly disturbed ecosystems (0.295 g m^{-3}) is also shown for reference.

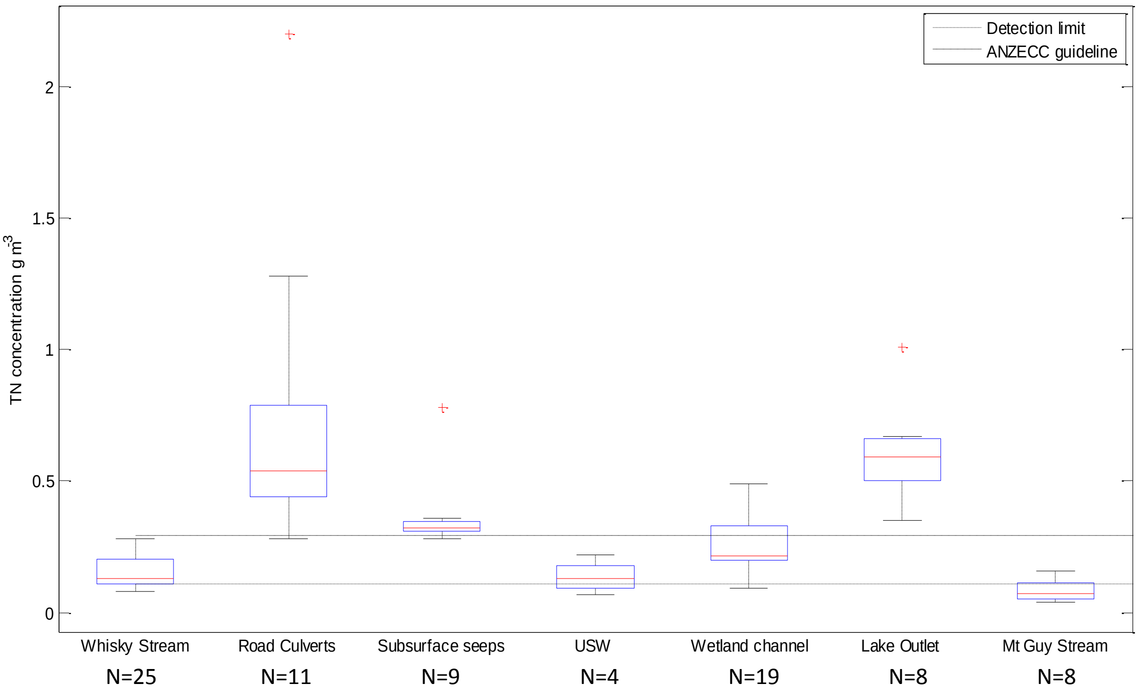

Figure 4-8, Box and Whisker plot of total nitrogen concentration in each key waterway.

Two un-impacted sites (MGS and USW) were sampled to determine a median natural baseline TN concentration in perennial streams, 0.079 g m^{-3} at MGS and 0.13 g m^{-3} at USW. These values are close to the median for Canterbury alpine-fed upland rivers (0.093 g m^{-3} Figure 4-11) (Stevenson et al. 2010). TN values for MGS, which drains unfarmed tussock grassland, were below the detection limit in 6 of 8 samples, and concentrations measured in the remaining three samples were well below the ANZECC guideline and the 95th percentile for Canterbury alpine-fed upland rivers of 0.32 g m^{-3} (Stevenson et al. 2010). USW is in the main wetland channel upstream of agricultural land use and has a similar natural tussock grassland catchment to Mount Guy Stream. This site had a median TN concentration higher than the median at MGS and only one sample of four was below the detection limit. However, there is no statistically significant difference in TN between these sites (Table 4-2). TN concentrations are as expected for upland natural streams and are not of concern.

Whisky Stream TN concentrations were consistently elevated above the natural baseline concentration but below the ANZECC guidelines and the 95th percentile for Canterbury alpine-fed upland rivers. No significant difference in TN concentration was seen between the three sites on Whisky Stream (Table 4-2). TN concentration was seen to increase in Whisky Stream during high flow but did not always (Figure 4-9). There was no strong overall correlation (R^2=0.1415) between flow and TN concentration and conditions other than the flow rate are believed to have had a greater effect on nitrogen concentration. Higher concentrations were seen in samples taken during the rising limb of a flow event. This was possibly due to near-stream sources of nitrogen being mobilised by surface runoff at the beginning of storm events. Specific conductance is elevated during the rising limb of a hydrograph in Whisky Stream (Figure 4-6) and decreases over the duration of the storm event. This indicates that dissolved solids, potentially including dissolved forms of nutrients, may be highest at the beginning of a storm event during the first flush. However, NH_4 and NNN concentrations did not have a strong correlation with SC (R^2=0.089 and 0.02 respectively).

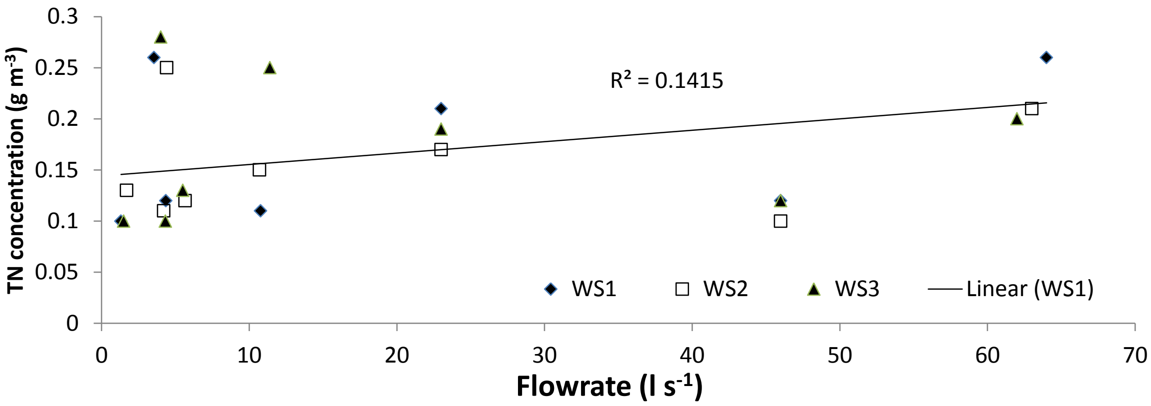

Figure 4-9, Scatter plot of total nitrogen concentration versus flow rate in Whisky Stream

TN concentration in the stormflow composite sample was consistent with concentrations recorded for grab samples taken in Whisky Stream on the 25th of May 2010. These grab samples were taken at the beginning of a large stormflow event after a long antecedent dry period. TN concentration in the composite sample (0.27 g m^{-3}) was 1.8 times that of the median concentration in Whisky Stream during baseflow (0.15 g m^{-3}). Inorganic nitrogen load did not increase considerably in Whisky Stream during storm events as NH_4 and NNN concentrations remained very low in the composite sample.

TN in the main wetland channel was consistently elevated from the natural baseline concentration and above the detection limit. TN concentration appeared to increase along the wetland channel from WC1 to WC3, although this trend is not statistically significant (p-value=1). In addition, TN concentration in the wetland channel was higher than all perennial tributaries flowing into the wetland. Increases in TN along the length of the wetland channel may be due to elevated NNN and TN concentration in subsurface lateral runoff (0.28-0.78 g m^{-3}) entering the wetland as it flows along the base of the farmed hillslope. Concentrations were highly variable in the channel; variation may be due to intermittent ephemeral flow (section 5.2). Groundwater nutrient loading into the wetland channel may also cause variation. No seasonal or inter-annual trends were evident in TN concentrations in the wetland channel. However, a longer monitoring period could provide evidence of seasonal trends.

TN concentration in Lambies Stream (lake outlet) consistently exceeded ANZECC guidelines for TN over the entire study period. TN concentration in the Lambies Stream (0.565 g m-3) was 2.6 times higher than in the wetland channel (0.22 g m-3), the only lake inlet downstream of farmland. The wetland channel is the only perennial surface water inlet to the lake downstream of farmland. This suggests an alternative source of nitrogen for Lake Clearwater. Alternate sources of nutrient loading into Lake Clearwater are discussed further in section 5.3.

Lambies Stream is at the outlet of Lake Clearwater and is assumed representative of the TN concentration in Lake Clearwater in this study. This assumption was supported by similarities between TN concentrations in Lambies Stream and ECan samples taken from the centre of the lake (Adrian Meredith personal communication 2012). Using ECan monitoring data and data from this study, Figure 4-10 shows an increase in TN concentration for Lake Clearwater from 2005 to 2012. Classification for Lake Clearwater changed from oligotrophic in 2005 to mesotrophic in 2007 (Enviroment Canterbury, 2008). Figure 4-10 shows the concentration of TN in Lake Clearwater increasing above the eutrophic threshold of 0.337 g m^{-3} (Burns et al. 2000).

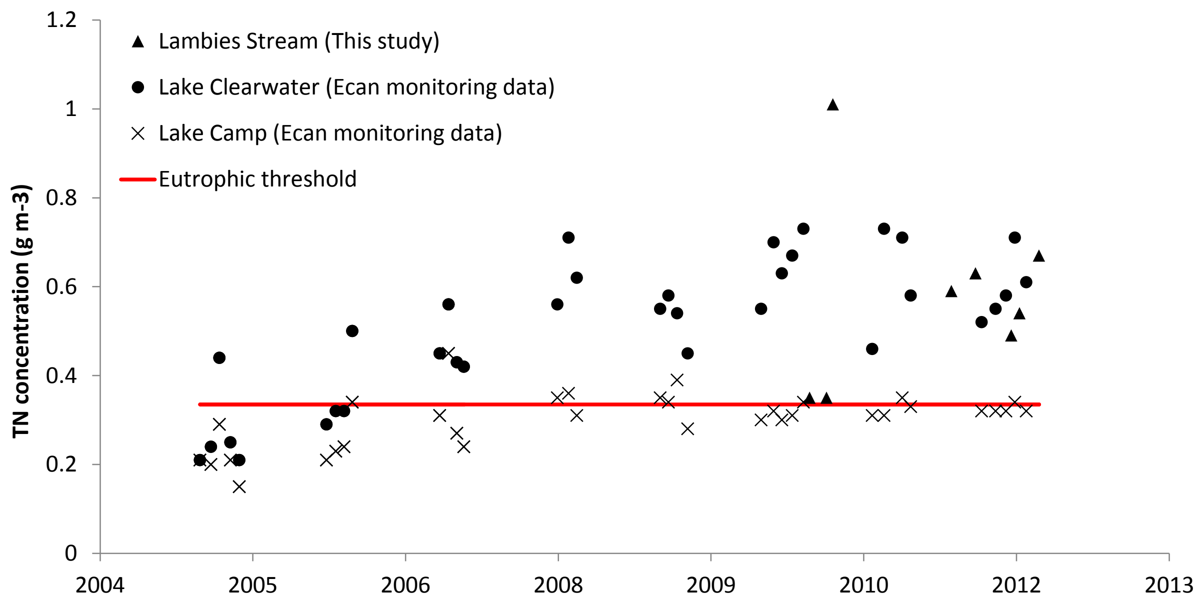

Figure 4-10, Graph of TN concentration in Lake Clearwater from summer 2005 to summer 2012.

TN concentration in perennial streams in the Lake Clearwater catchment is compared with concentration in different types of Canterbury rivers and with hill-fed and lake-fed inlets to Lake Hayes (Bayer et al. 2008) in Figure 4-11. Medians are shown as a vertical line within a horizontal range. Median TN concentration is elevated in the Lake Clearwater catchment, compared to upland rivers in Canterbury

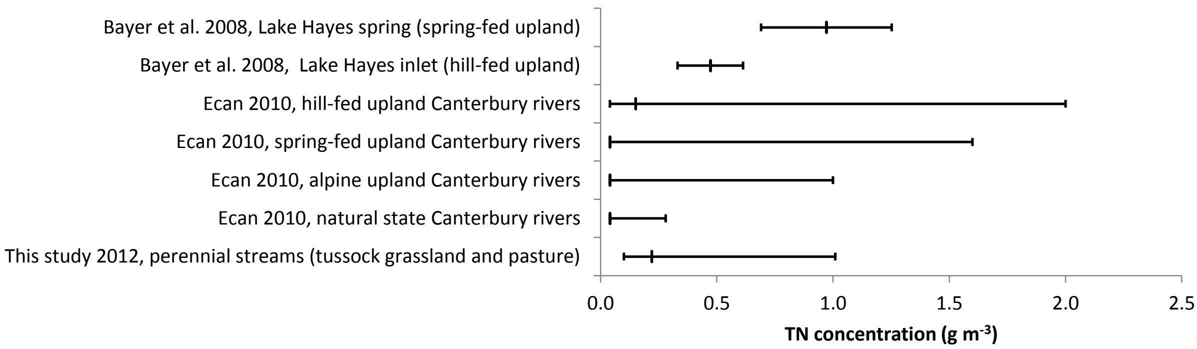

Figure 4-11, Comparison of perennial stream TN concentrations found in this study to other studies

TN concentrations are above median values for upland Canterbury Rivers but below maximum values found. TN concentrations are also below, but comparable to, concentrations found in tributaries of Lake Hayes, a eutrophic upland lake impacted by agricultural and residential nitrogen sources (Bayer et al. 2008).

4.3.2 Ammoniacal nitrogen (NH_4-N)

The detection limit of 0.01 g m^{-3} for ammoniacal nitrogen is also the ANZECC trigger value for ammoniacal nitrogen in New Zealand upland rivers with slightly disturbed ecosystems. Only 20% of 73 samples (shown in Figure 4-12) were above this detection limit. Concentration is high, up to 0.115 g m^{-3} (11 times the trigger value), at the ephemeral culverts (RC1, 2 and 3) during the rising limb of a high flow event on the 25th of May 2012. Before this storm, a long period of dry weather is likely to have caused sources of ammoniacal nitrogen, such as urine and faeces, to accumulate in farmland ephemeral channels while the channel was dry. High concentrations in this sampling event are likely to represent a first flush of nutrients. Concentrations up to four times the trigger value (0.035 g m^{-3}) were also found, in Whisky Stream (WS1, 2 and 3) and the wetland channel (WC1 and 2), during storm flow events in November 2011 and March 2012. The cause of greater concentrations during these sampling events was not clear, but increases could be related to changes in farming activity up stream. Ammoniacal nitrogen is less mobile in soil, due to its reduced state, than nitrate and this may limit leaching and near stream losses in this catchment, which has relatively low rainfall and erosion. In addition, ammoniacal nitrogen is readily bioavailable and is likely to be rapidly converted to organic forms of nitrogen in-stream. The proportion of ammoniacal nitrogen in TKN increased during some heavy rainfall and high flow events. This suggests that the primary loss pathways for ammoniacal nitrogen were erosion and overland flow from near-stream sources.

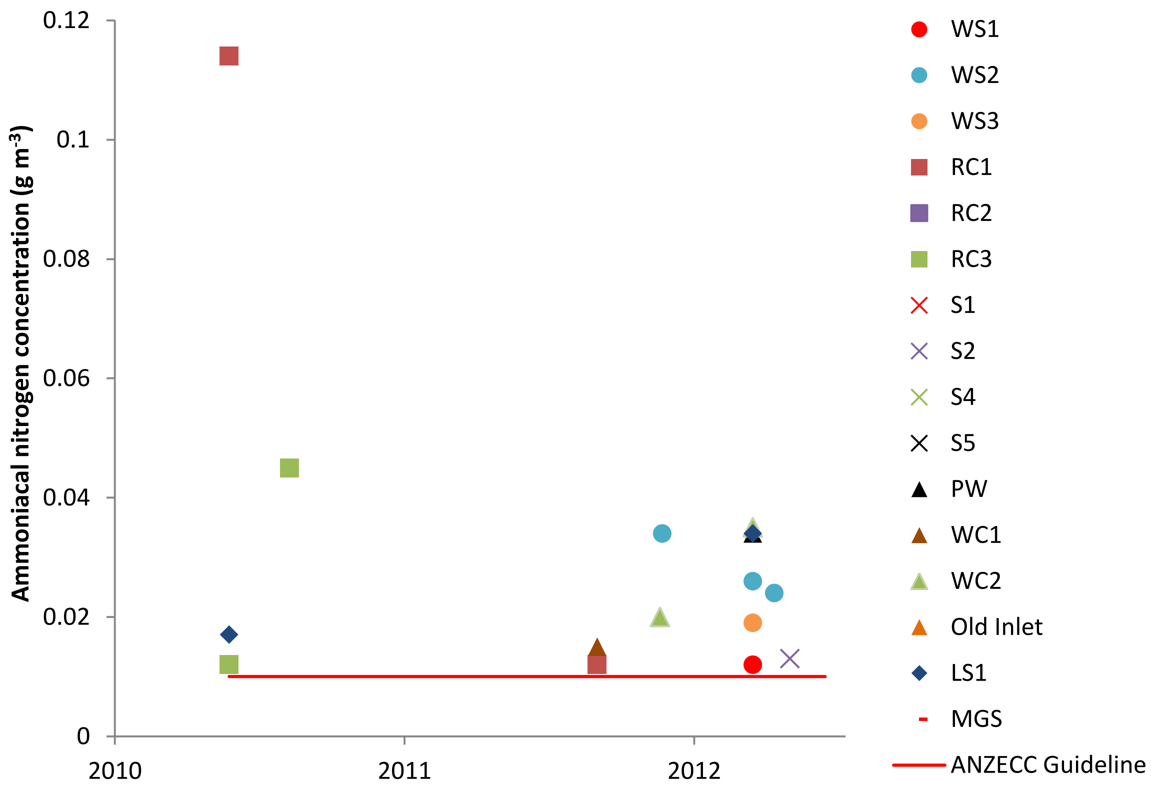

Figure 4-12, Ammoniacal nitrogen concentration for all samples above the detection limit

4.3.3 Nitrate and nitrite (NO_3^- and NO_2-N)

Nitrate (NNN) concentration across all sites for all sampling events is shown in Figure 4-13. The combined NNN concentrations from test results were assumed to be predominantly nitrate as it is uncommon for nitrite to be a stable compound in natural waters (Burt et al. 1993). NNN is shown as a scatter plot as the sample size for individual subsurface seeps was insufficient for a box plot.

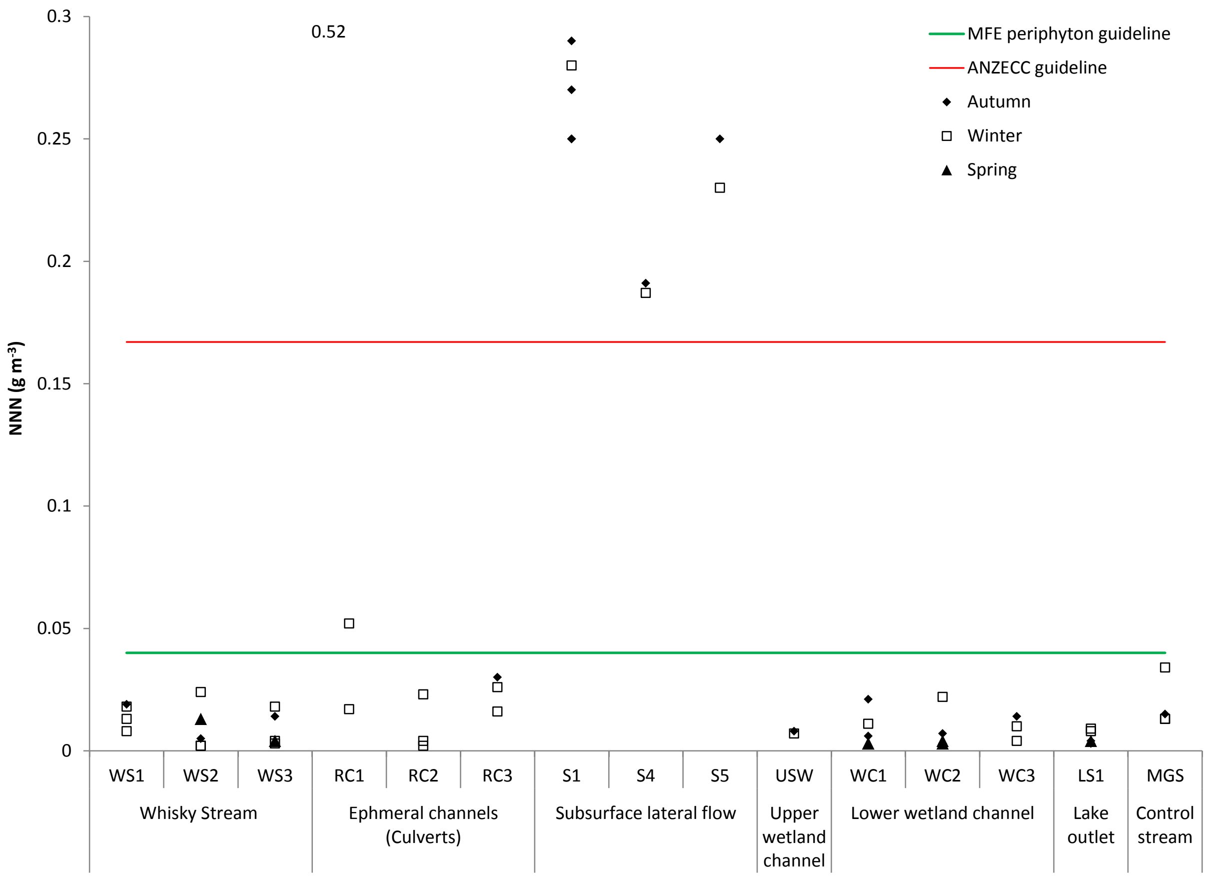

Figure 4-13, Scatter plot of all sampling events showing spatial variability of NNN concentration. One high concentration in RC1 is shown as a numerical value.

The ANZECC trigger value, 0.167 gm^{-3}, for NNN in upland rivers in New Zealand with slightly disturbed ecosystems is shown. Nitrate was well below the ANZECC guideline for all surface water samples, but one. Nitrate in surface waters was also typically below the Ministry for the Environment dissolved inorganic nitrogen (DIN) guideline (0.04 – 0.10 g m^{-3}) for nuisance periphyton growth (Ministry For the Environment 1992). This guideline states that if DIN is below this range periphyton biomass is expected to decrease. The only exception is two samples from RC1, one of which was very high (0.52 g m^{-3}).

It is common for nitrate to be the primary nitrogen species present in runoff from farmland due to the high solubility, and mobility, of this ion (Burt et al. 1993). Nitrate was only a small part of TN in surface water. This indicated that nitrate entering surface water was rapidly assimilated and transformed into organic forms of nitrogen. In contrast, nitrate was the dominant component of TN in subsurface water seeps. The median nitrate content in TN in surface water was 11%, but in subsurface water seeps it was 74%. It is noted that while the seep concentrations were higher than the ANZECC guideline value, concentrations are still well below the maximum acceptable value (MAV) of 11.3 g m^{-3} set by the Ministry of Health for drinking water (Ministry of Health 2008). Subsurface runoff was not a human drinking water source but could be a source of water for livestock and other animals. Nitrate concentrations in the seeps were also below nitrate concentrations in a spring fed inlet to Lake Hayes (Figure 4-14). NNN transported by the subsurface runoff is thought to be the reason for increasing TN concentration in the wetland channel at the base of the farmed hillslope and NNN in subsurface runoff is thought to make a large contribution to elevated TN concentration into the wetland.

NNN concentration, in perennial streams in the Lake Clearwater catchment, is compared with concentration in different types of Canterbury rivers and with hill-fed and lake-fed inlets to Lake Hayes (Bayer et al. 2008) in Figure 4-14. Median nitrate concentration for this study was below concentrations found in Canterbury Rivers and streams flowing into to Lake Hayes. The median NNN concentration is at the low end of the range because all surface water samples had low concentrations. The higher concentrations in the range shown for this study are all from subsurface samples.

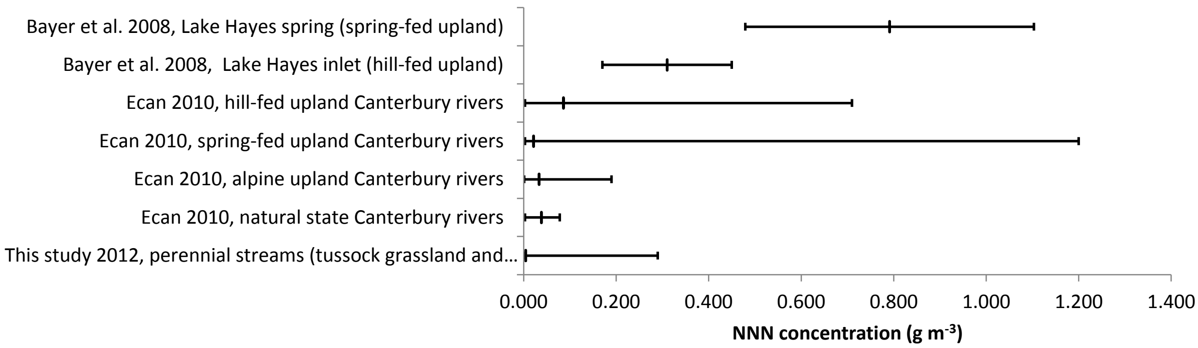

Figure 4-14, Comparison of perennial stream NNN concentrations found in this study to other studies (Medians are shown as a vertical line within a horizontal range)

4.3.4 Total Kjeldahl nitrogen (TKN)

TKN is the sum of ammoniacal nitrogen and organic nitrogen. Six samples had between 10% and 21% ammoniacal nitrogen. However, ammoniacal nitrogen was typically less than 10% of TKN in all sampling events; the majority was organic nitrogen. TN was predominantly organic nitrogen in most samples with the exception of samples from the subsurface seeps. Nitrate was the dominant species in the seeps. For all other waterways, organic nitrogen is the dominant form of nitrogen.

4.3.5 Total phosphorus (TP)

TP concentrations in waterways for all sampling events are summarized in Figure 4-15. The ANZECC trigger value for TP in upland rivers in New Zealand with slightly disturbed ecosystems (0.026 g m^{-3}) is also shown for reference.

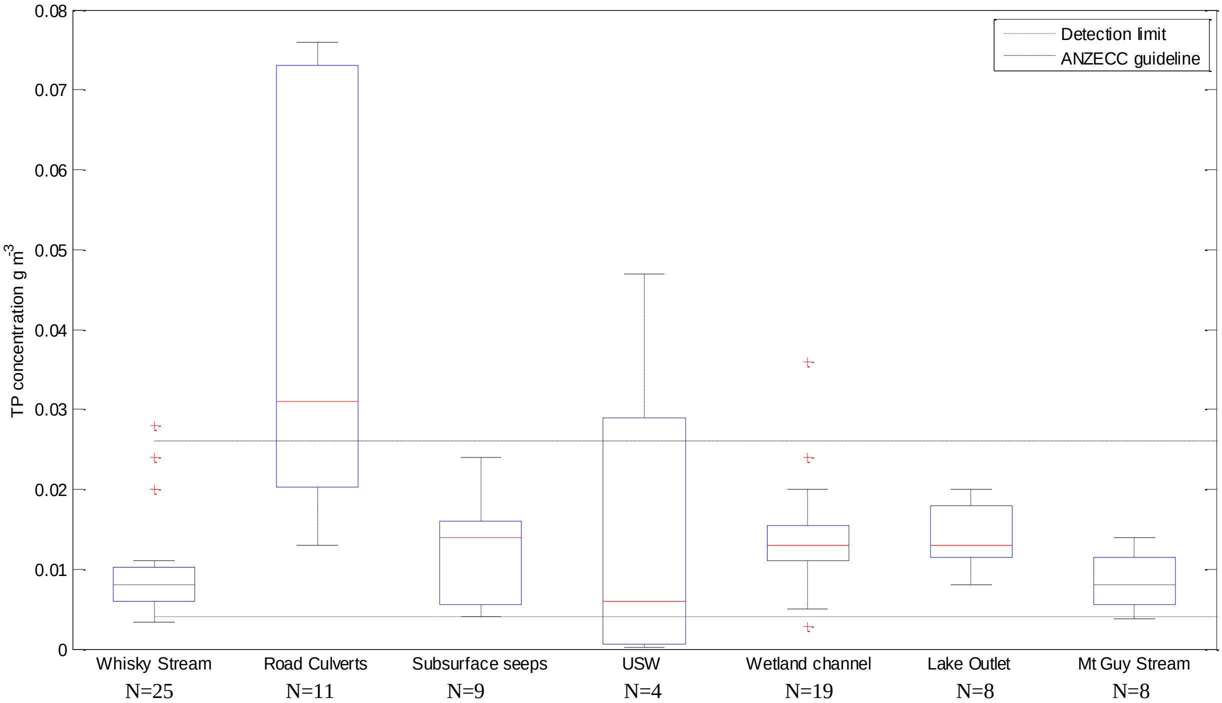

Figure 4-15, Box and Whisker plot of TP concentration in each key waterway

TP was elevated in the ephemeral channels draining agricultural land, with a median value of 0.03 g m^{-3}. The source of TP in these channels is expected to be via direct input of animal waste as well as erosion due to pugging within the channels feeding the culverts. Animals have direct access to the channels on farmed land and gather in these areas to drink from the channels.

The two median TP concentrations found for un-impacted streams were 0.008 g m^{-3} at MGS and 0.007 g m^{-3} at USW. TP median and mean concentration in natural rivers in Canterbury was 0.004 g m^{-3} and 0.007 g m^{-3} respectively (Environment Canterbury 2012). Median TP concentration at Whisky Stream was 0.08 g m^{-3}. However, higher concentrations were measured during one flow event in Whisky Stream on the 25th of May 2010. TP concentration in the stormflow composite sample was consistent with concentrations recorded for grab samples taken in Whisky Stream on the 25th of May 2010. These grab samples were taken at the beginning of a large storm event after a long antecedent dry period and are representative of the rising limb of the storm hydrograph. TP concentration in the composite sample (0.02 g m^{-3}) was approximately double the median concentration in Whisky Stream during baseflow (0.009 g m^{-3}). This is expected as phosphorus commonly mobilizes with sediments in high flow events (Alexander et al. 2002; Caruso 2000). Although TP concentration did increase during this high flow event this was not always the case. Figure 4-16 shows the lack of correlation between TP concentration and flow rate in Whisky Stream.

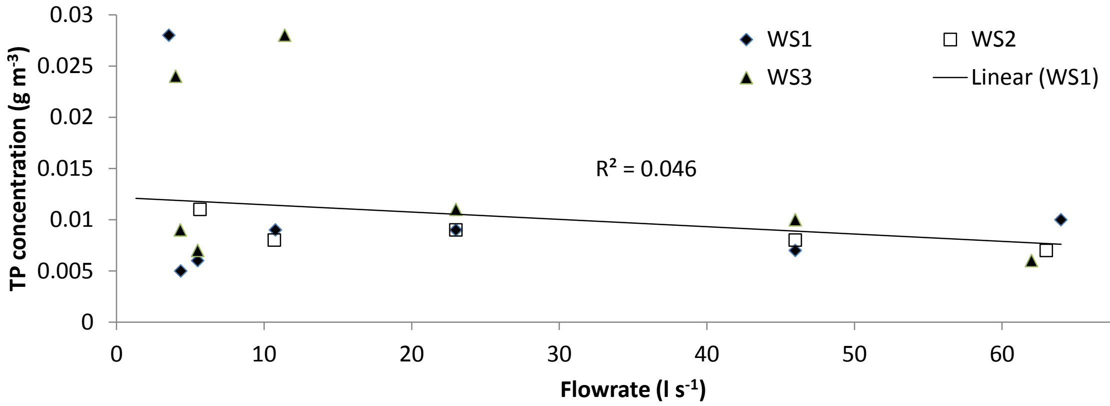

Figure 4-16, Scatter plot of TP concentration versus flow rate in Whisky Stream

Median TP concentration was similar for subsurface seeps (0.014 g m^{-3}), the wetland channel (0.013 g m^{-3}) and the outlet of the lake (0.013 g m^{-3}). No seasonal or inter-annual trends were evident in TP concentrations in the wetland channel or lake outlet. Although concentration in these waterways was higher than streams draining natural land, it was still well below ANZECC guidelines and within normal ranges for natural upland streams in Canterbury. TP concentration in perennial streams in the Lake Clearwater catchment, is also comparable to concentrations found in other upland Canterbury rivers and with hill-fed and lake-fed inlets to Lake Hayes (Bayer et al. 2008) in Figure 4-17.

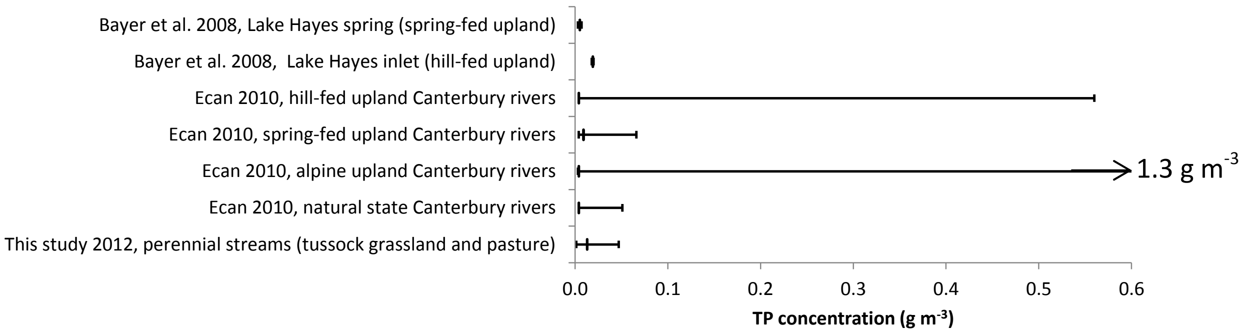

Figure 4-17, Comparison of perennial stream TP concentrations found in this study to other studies (Medians are shown as a vertical line within the horizontal range)

Comparison with similar waterways and guidelines suggests that phosphorus in runoff from farmland may not be as much of a concern as nitrogen in the Lake Clearwater catchment. However, phosphorus may be a limiting nutrient for phytoplankton growth in Lake Clearwater (section 4.3.7). If so, increases in phosphorus concentration in Lake Clearwater would be likely to increase the trophic status of the lake (section 1.3).

TP concentrations for ECan samples, taken form the centre of the lake, and samples from Lambies stream (this study) are shown in (Figure 4-18). TP concentration has roughly tripled in Lake Clearwater from 2004 to 2012. TP concentration appears to be higher in the centre of the lake than in Lambies Stream. This may indicate TP, which is typically bound to sediment, was attenuated by settling of sediment along the length of the lake. In 2012 TP concentration was close to the lower threshold given for a eutrophic lake in Burns et al. (2000).

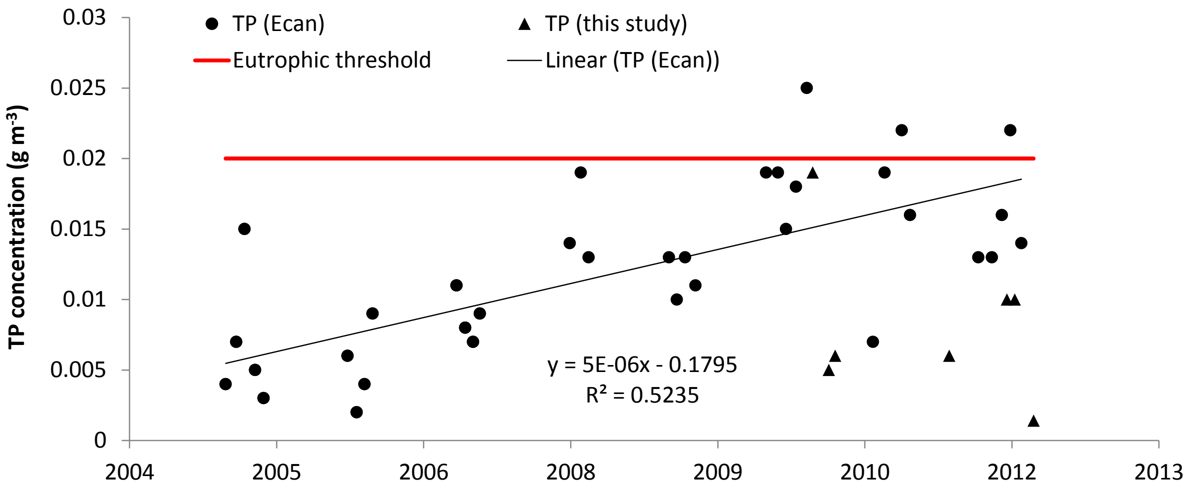

Figure 4-18, Scatterplot of TP concentration in Lake Clearwater from 2004 to 2012

4.3.6 Dissolved reactive phosphorus (DRP)

Dissolved reactive phosphorus (DRP) was below the detection limit for 83% of 73 samples. Figure 4-19 shows a scatter plot of all samples above the detection limit and indicates concentrations are higher during large storm events. For example, samples from the 25th of May 2010 were elevated and taken during a large storm event in late autumn after a long period of low flows. DRP concentration in the stormflow composite sample at WS2 was just above the detection limit (0.004 g m^{-3}), approximately half the concentrations recorded on the 25th of May 2010 in WS2. Baseflow samples at all sites have DRP concentrations below detection limits.

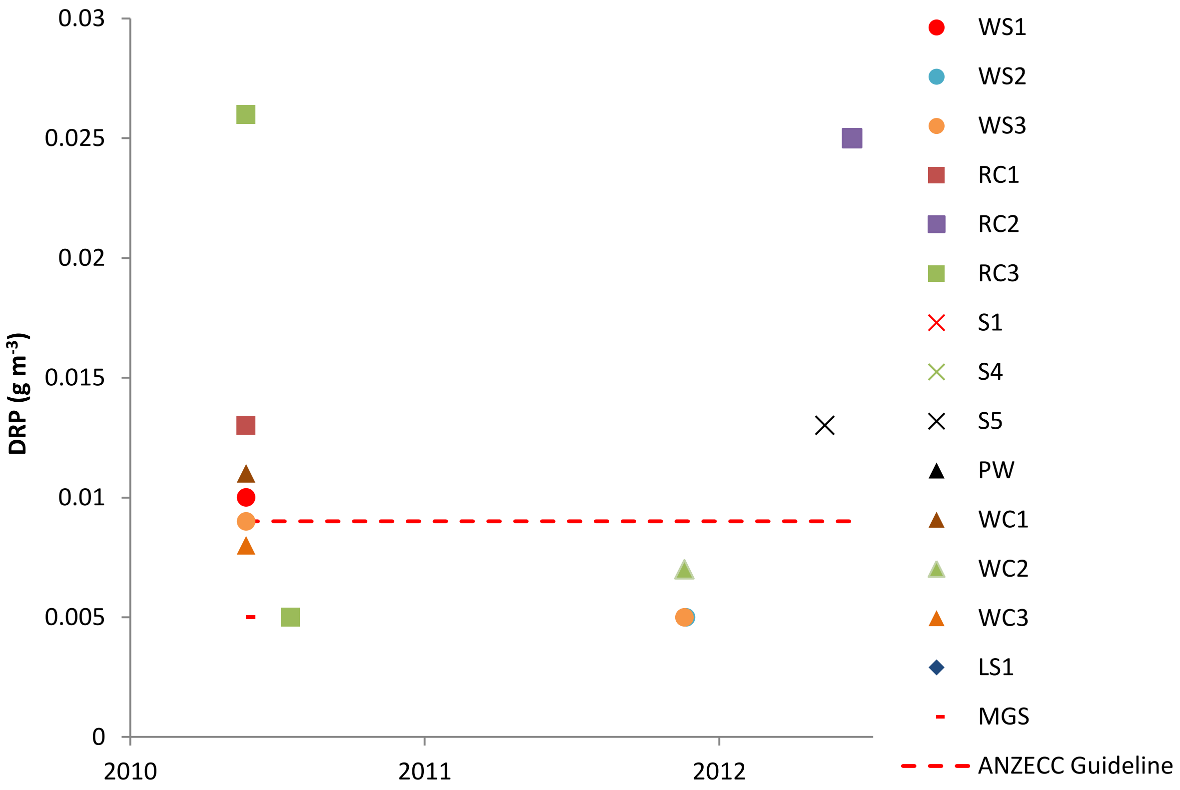

Figure 4-19, Dissolved reactive phosphorus across all monitoring sites for all sampling events (One high concentration of 1 g m^{-3} at RC2 (25/5/2010) is not shown)

DRP was generally below the ANZECC guideline of 0.0095 g m^{-3} (Figure 4-19 and Figure 4-20). DRP was also below the 2002 national median value (0.006 g m^{-3}) for rivers and streams with less than 25% agricultural land use (Ministry For the Environment 2007). Apart from two samples, DRP in surface waters was also below the Ministry for the Environment guideline (0.015 – 0.030 g m^{-3}) for nuisance periphyton growth (MfE, 1992). DRP concentrations for all samples across all sites are also shown in Figure 4-20 to highlight spatial variation. Data are not shown as boxplots because the sample size at each site was not sufficient. Like TP, DRP was highest in the ephemeral culverts.

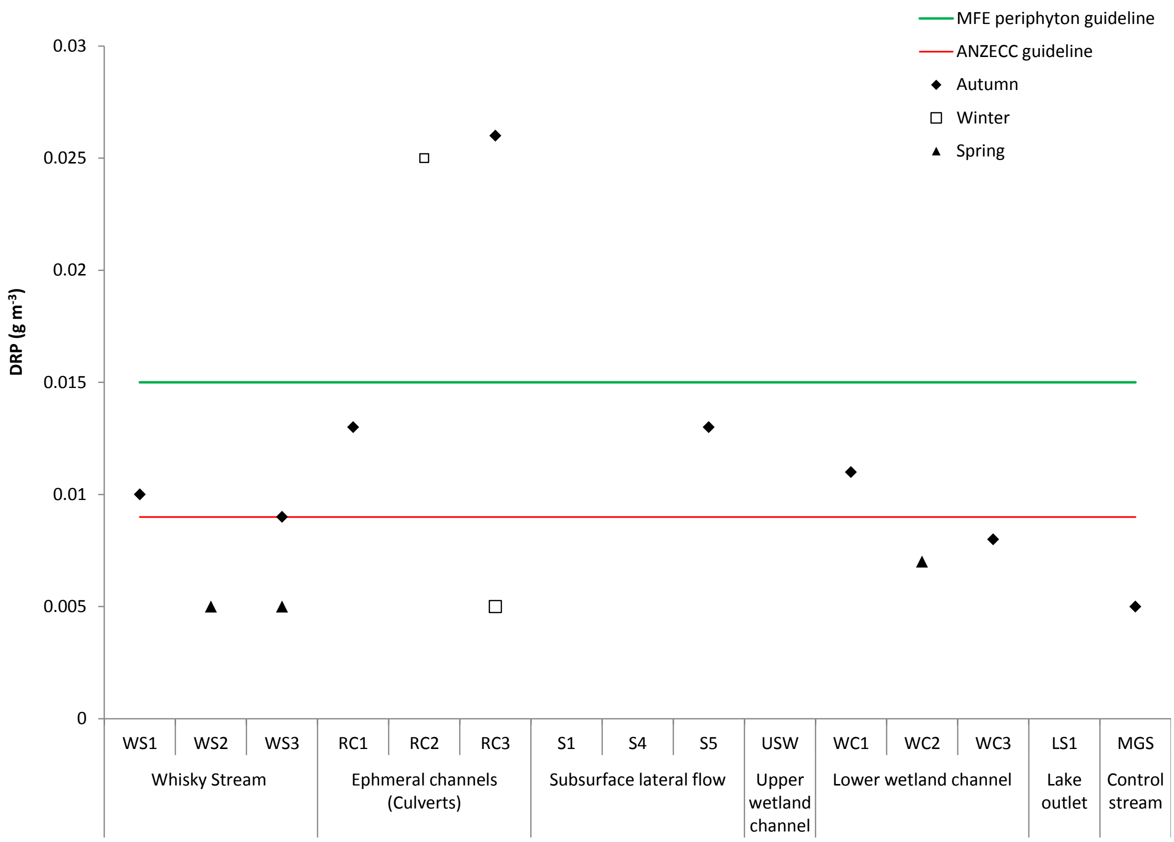

Figure 4-20, DRP concentration across all sampling sites for all sampling events

DRP concentrations in perennial streams in the Lake Clearwater catchment, were compared with concentration in different types of Canterbury rivers and with hill-fed and lake-fed inlets to Lake Hayes (Bayer et al. 2008) in Figure 4-17. Minimum DRP concentrations in this study were above the minimum concentrations found in studies included in Figure 4-21. However, the minimum for this study is also the detection limit and non-detects are not included in this range. The actual minimum for this study is very likely to be well below 0.004 g m^{-3} as 82% of samples had DRP concentrations below the detection limit. The median DRP concentration calculated for samples above the detection limit would be unrealistically high due to the large number of non-detects. Therefore, the median is not shown for this study.

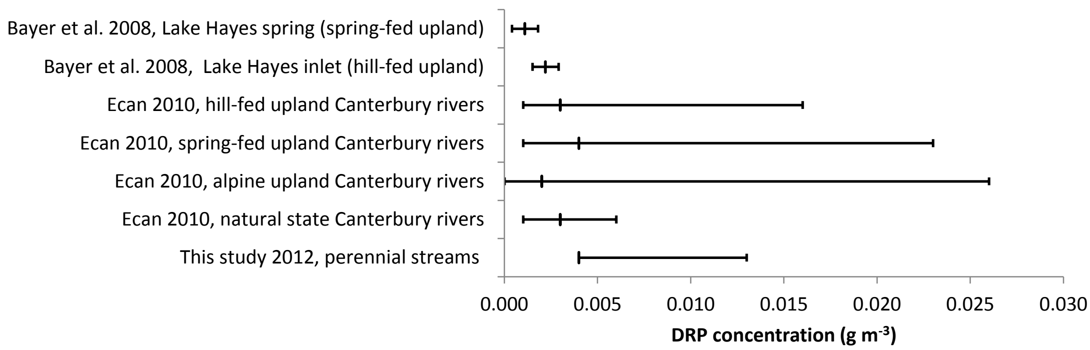

Figure 4-21, Comparison of perennial stream DRP concentrations found in this study to other studies (Medians are shown as a vertical line within a horizontal range)

4.3.7 Lake Clearwater nutrient limitation

Comparison of the ratio of TN and TP in lake water with the nutritional requirements of phytoplankton can indicate if growth is limited by TN, TP or both nutrients. The accepted TN:TP ratio for balanced growth is 7.2:1 by mass (16:1 by mole) (Abell et al. 2010). The median TN:TP ratio in Lake Clearwater was 49:1, from 2004-2012. TN:TP above 15:1 is assumed, in Abell et al. (2010), to indicate phosphorus limitation. Lake Hawdon, another Canterbury high country lake 84 km northeast of Lake Clearwater at 579 m above sea level, also had a very high TN:TP ratio (89.7:1) (Abell et al. 2010). This indicates that Lake Clearwater and other Canterbury high country lakes may be phosphorus limited. Measures to limit phosphorus and sediment load into the lake may be helpful to limit the productivity of Lake Clearwater. Further work to ascertain the actual nutrient limitation status of Lake Clearwater would also be useful for managing water quality in the lake.

Table 4-7, Annual average TN and TP concentration and TN:TP ratios for Lake Clearwater

Year	Number of samples	TN (g m^{-3})	TP(g m^{-3})	TN:TP
2004	2	0.21	0.004	53
2005	8	0.29	0.008	46
2006	8	0.36	0.005	86
2007	8	0.47	0.009	55
2008	3	0.63	0.015	42
2009	5	0.53	0.013	42
2010	8	0.61	0.014	58
2011	6	0.63	0.015	49
2012	7	0.59	0.012	43
			Median	49

5 Nutrient loads and yields

This section presents the estimated nutrient loads in the Lake Clearwater catchment and discusses potential sources of additional nutrient load into the lake. Annual nutrient loads and yields were calculated from July 2011 to June 2012.

5.1 Annual nutrient loads and yields

Total annual measured TN loads are shown in Figure 5-1. This figure shows total measured load as the sum of natural load and load resulting from agricultural land use. The left and right column for each site both show the same total load but the left column shows a low estimate of natural load from unfarmed land for each catchment and the right column shows a high estimate of load from unfarmed land.

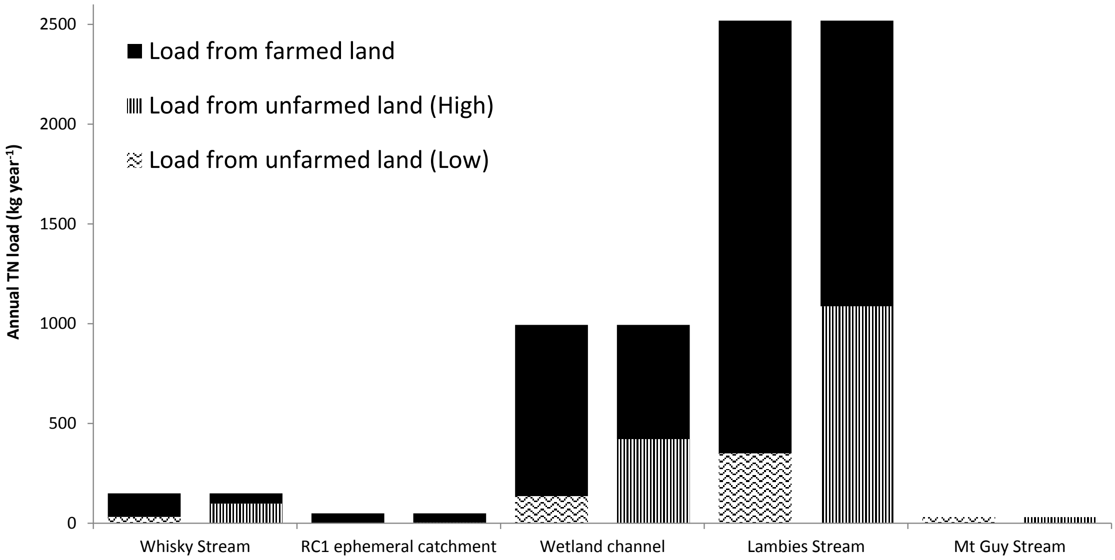

Figure 5-1, TN loads in monitored surface waterways

Loading from RC1 and other ephemeral flow is very seasonal as the ephemeral channels flow only during wet periods, generally winter and spring, and large rainfall events. Natural load was low in RC1 because 77 % of RC1's catchment was farmed land. Natural load in other catchments was a considerable proportion of the total load because only a small area of the total catchment was farmed (Table 1-2). All loading at MGS was natural, as the catchment contained no farmed land.

Subsurface TN load from the farmed hillslope catchment into the wetland (Figure 2-18) was calculated to be between 236-443 kg year^{-1}. Total surface water TN load (perennial and ephemeral streams) from the farmed hillslope into the wetland was calculated to be 382 kg year^{-1}. Total load in the wetland channel was 994 kg year^{-1}. The remaining load in the wetland channel was natural loading from the unfarmed land north of the valley floor.

Figure 5-2 shows calculated TN yields for the farmed land within each catchment. Yields from farmland in the perennial Whisky Stream catchment (0.71-1.64 kg ha^{-1} year^{-1}) and ephemeral stream catchments (1.3-1.35 kg ha^{-1} year^{-1}) were similar, but only roughly half the total yield for farmland

(1.96-2.94 kg ha^{-1} year^{-1}). The remaining yield from the farmed hillslope was assumed to come from subsurface nitrogen load (0.81-1.52 kg ha^{-1} year^{-1}). Yields from surface and subsurface runoff each represented roughly half of the total yield from the farmed hillslope. Using the estimated subsurface yield, total subsurface load from all farmland in the Lake Clearwater catchment was calculated to be between 338 and 634 kg year^{-1}.

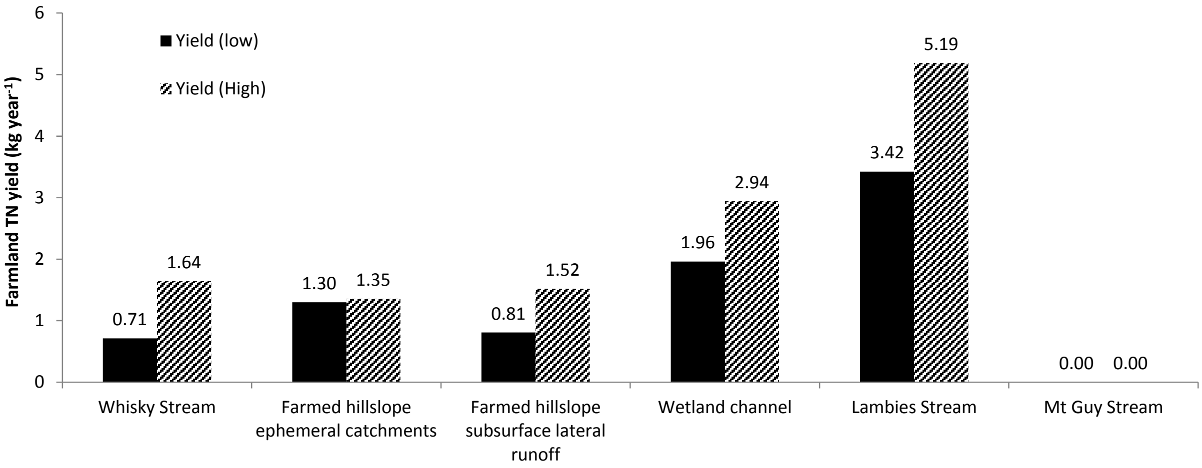

Figure 5-2, TN yields from farmed land

The TN yield for farmed land calculated at the wetland channel (1.96-2.94 kg ha^{-1} year^{-1}) was only 57 % of the yield calculated for farmland at LS1 (3.42-5.19 kg ha^{-1} year^{-1}). Other unmeasured sources of nutrients into the lake (section 5.3) are thought to be the reason this yield was higher than the yield calculated in the wetland channel. The difference in yields provided an estimate of unaccounted for load into Lake Clearwater of 611-939 kg year^{-1}.

The Proposed Canterbury Land and Water Regional Plan (Environment Canterbury 2012) has set a limit of 20 kg ha^{-1} year^{-1} of nitrogen loss from farms. Nitrogen losses above this will require resource consent. Farms in a sensitive lake catchment, such as Lake Clearwater, have been required to comply with this limit since 11th of August 2012. Results show that farming nitrogen losses in the Lake Clearwater catchment (1.96-2.94 kg ha^{-1} year^{-1}) are not likely to reach this limit.

Measured TN yields are compared to yields calculated in other studies for pastoral land use in New Zealand and internationally by Young et al. (1996) in Figure 5-3. Measured yields, in the Lake Clearwater catchment are shown to be in the lower end of the range for TN yields for non-dairy pastoral land use. The range of TN yields calculated from load in the wetland channel (1.96-2.94 kg ha^{-1} year^{-1}) was expected to be the total yield from farmland in the Lake Clearwater catchment, as it contains both surface and subsurface nutrient load. The upper range of this yield corresponds with the lowest value given in Elliot and Sorrell (2002) for pastoral land use (2.8 kg ha^{-1} year^{-1}). Yield found in this study were well below yields found for lowland agricultural pastoral land use in New Zealand (Cooper and Thomsen 1988; Quinn and Stroud 2002).

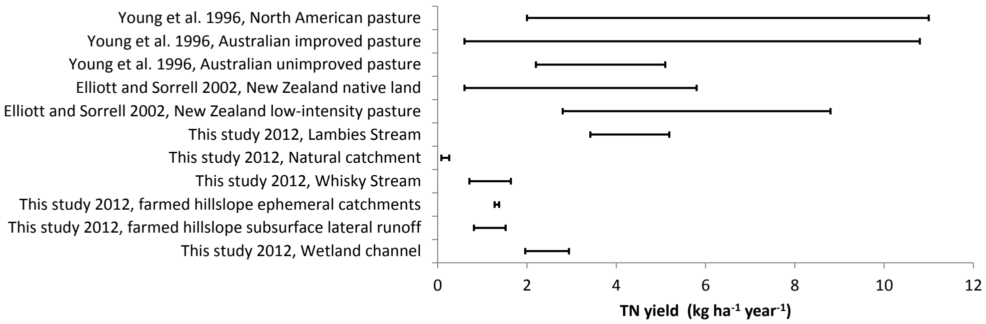

Figure 5-3, Comparison of annual TN yields to other studies

Total annual measured TP load is shown in Figure 5-4. Like TN, this figure shows total measured load as the sum of natural load and load resulting from agricultural land use. The left and right column for each site both show the same total load but the left column shows a low estimate of natural load from unfarmed land for each catchment and the right column shows a high estimate of load from unfarmed land. Subsurface TP load from the farmed hillslope into the wetland channel (Figure 2-18) was calculated to be between 10-16 kg year^{-1}. Total surface water (ephemeral and perennial streams) TP load from the farmed hillslope into the wetland was calculated to be 16 kg year^{-1}. Total load in the wetland channel was 50 kg year^{-1} and the remaining load in the wetland channel was natural loading from the unfarmed area north of the valley floor. Measured TP load at the lake outlet was close to the estimated natural load for the Lake Clearwater catchment. This may indicate that TP load was attenuated in the lake.

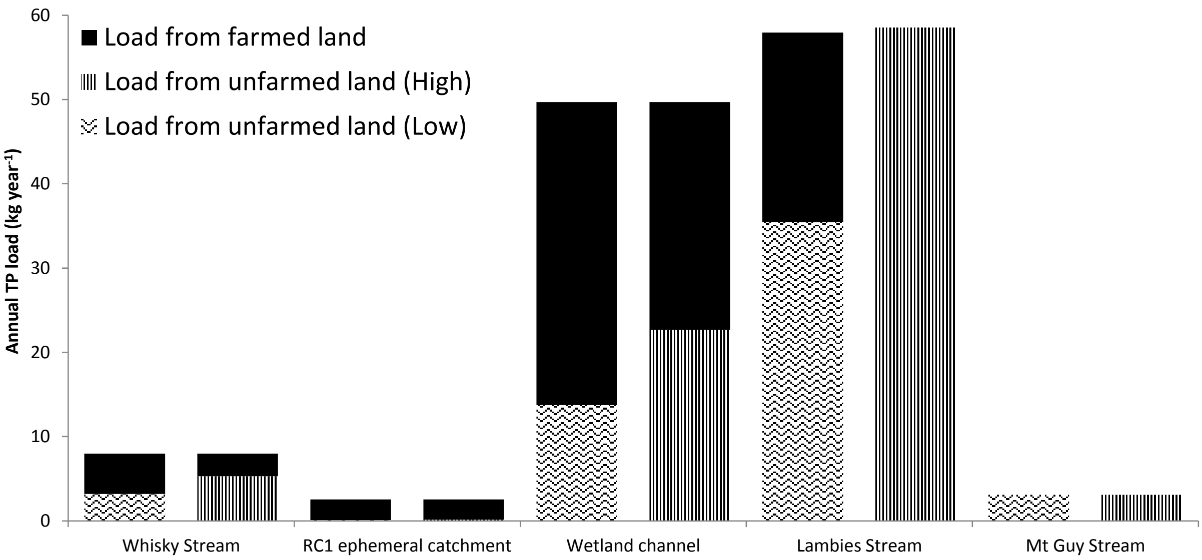

Figure 5-4, TP loads in monitored surface waterways

Figure 5-5 shows calculated TP yields for the farmed land within each catchment. The TP yield calculated for the ephemeral RC1 catchment (0.067-0.069 kg ha^{-1} year^{-1}) was higher than the yield for farmland in the perennial Whisky Stream catchment (0.037-0.069 kg ha^{-1} year^{-1}). Both the RC1 and Whisky Stream catchment farmland yields were well below the total yield for farmland (0.093-0.123 kg ha^{-1} year^{-1}), calculated from the load in the wetland channel. The remaining yield was assumed to come from subsurface runoff from the farmed hillslope (0.033-0.055 kg ha^{-1} $year^{-1}$). Subsurface flow accounted for approximately 30% of the total TP yield from the farmed hillslope.

TP yield from farmland calculated at Lambies Stream was very low. This was likely due to attenuation of phosphorus in Lake Clearwater. Phosphorus attenuation of around 30% is common in lakes (Kõiv et al. 2011). Settling of phosphorus bound to sediment is a likely cause of attenuation in Lake Clearwater. Phosphorus is also taken up during organic matter production in lakes and can be re-mineralized when organic matter containing phosphorus decomposes on the lake bed (Harding et al. 2004).

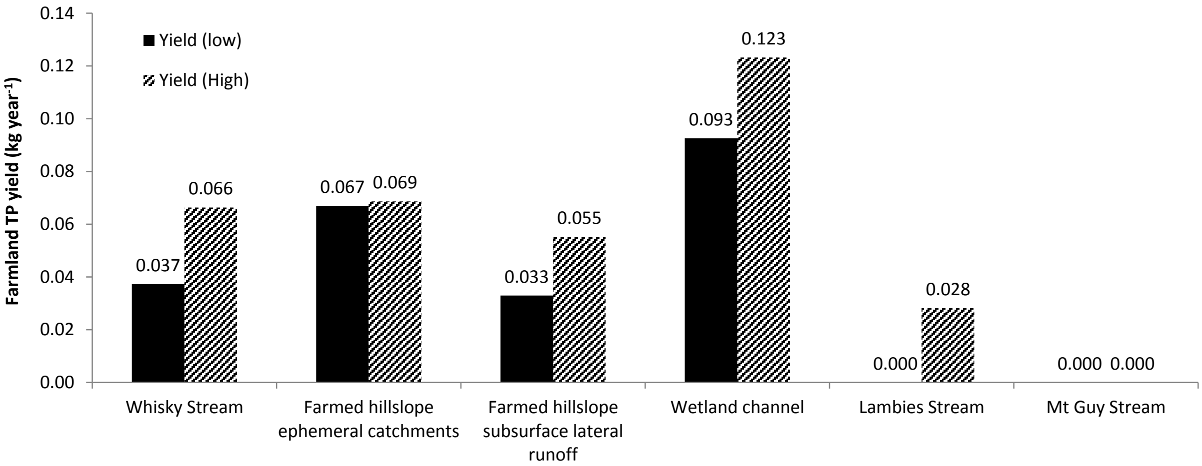

Figure 5-5, TP yields from farmed land

Measured TP yields are compared to yields calculated in other studies for pastoral land use in New Zealand and internationally in Figure 5-6. The TP load calculated at the wetland channel for farmed land (0.093-0.123 kg ha^{-1} $year^{-1}$) was similar to the minimum value (0.12 kg ha^{-1} $year^{-1}$) found for native catchments but approximately a third of the minimum value found for low intensity pastoral agriculture (0.3 kg ha^{-1} $year^{-1}$) given by Elliott and Sorrell (2002). TP yield in the Lake Clearwater catchment was also low compared to Australian and North American values. However, yield from farmland (0.093-0.123 kg ha^{-1} $year^{-1}$) was much higher than natural yield (0.0085-0.014 kg ha^{-1} $year^{-1}$) in the Lake Clearwater catchment.

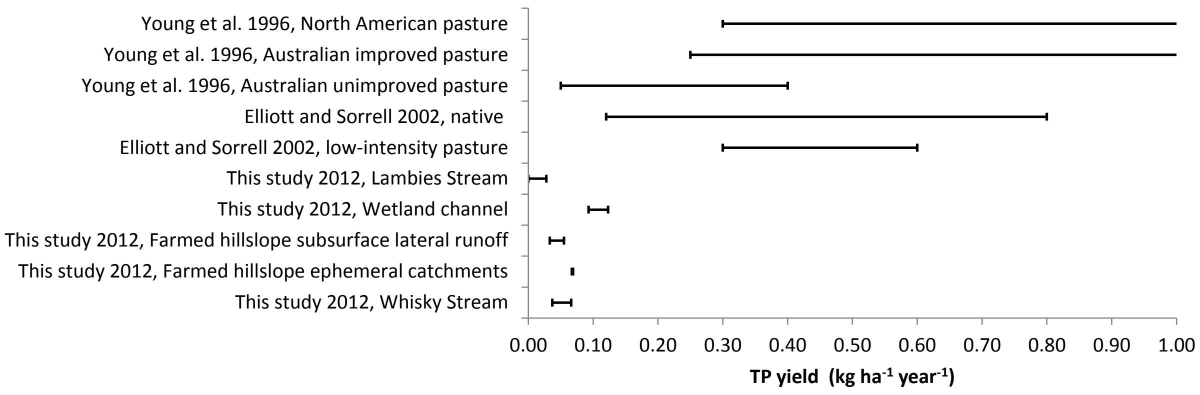

Figure 5-6, Comparison of annual TP yields to other studies

A summary of estimated TN and TP loads in the Lake Clearwater catchment is shown in Figure 5-7. This figure estimates diffuse nutrient loads from farmed and un-farmed land. Sources of nutrient loading that may be important not included in this schematic are discussed in Section 5.3.

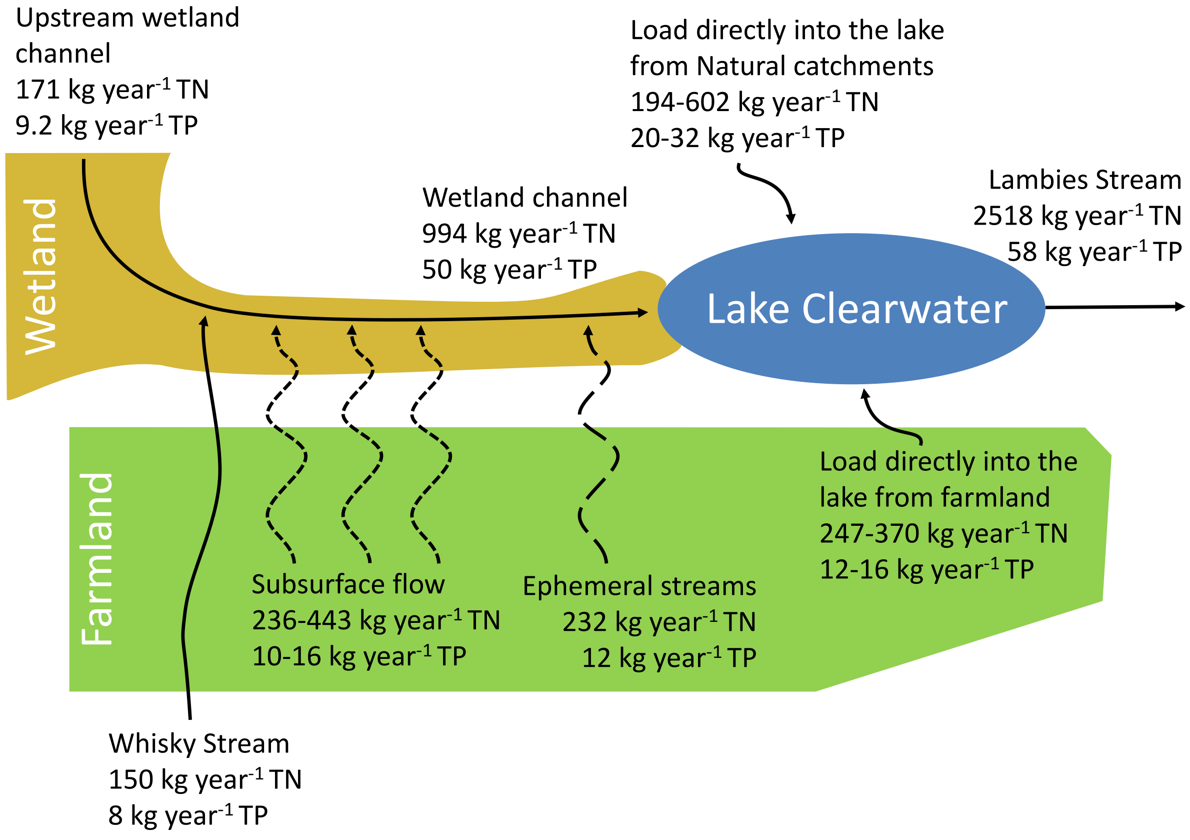

Figure 5-7, Schematic of estimated loads in Lake Clearwater waterways

5.2 Instantaneous nutrient loads

Sampling data was insufficient to calculate reliable seasonal load estimates. To investigate differences in loading between seasons, concurrent instantaneous loads were calculated to contrast loads during dry autumn conditions and wet spring conditions. Instantaneous nutrient loads were evaluated for a spring and an autumn sampling event to investigate differences in loading between dry autumn (11/4/2012) and wet spring (19/11/2011) conditions. During summer and autumn, the ephemeral channels were generally dry and inundated wetland area was reduced. During winter and spring, ephemeral channels flow and much of the wetland becomes inundated.

During wet conditions, ephemeral flow was a large proportion of TN and TP load entering the wetland (Figure 5-8 and Figure 5-9). Measured load in the wetland channel was also greater on the 19th of November 2011 when ephemeral flow existed. Additional loading in the wetland channel above measured surface water inputs was assumed to come from farmland sources via subsurface runoff; however, seasonal release of nutrients from the wetland itself could be an important source of nutrients (Peters and Clarkson 2010).

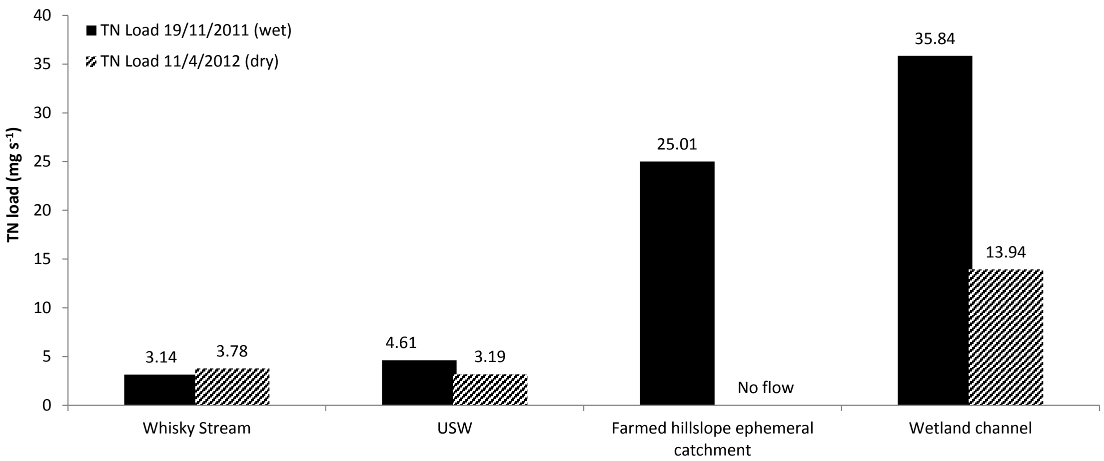

Figure 5-8, Instantaneous TN loads for 19/11/2011 and 11/4/2012

Estimates of the instantaneous load in Whisky Stream and the wetland channel are expected to be reasonably accurate because both flow rate and nutrient concentration were directly measured. Whereas, the assumption that runoff and nutrient concentration at RC1 was representative of all ephemeral catchment on the farmed hillslope introduces considerable uncertainty into the ephemeral load estimates shown in Figure 5-8 and Figure 5-9. However, the estimate of ephemeral load is useful to show the relatively large contribution ephemeral flow makes to load during wet conditions.

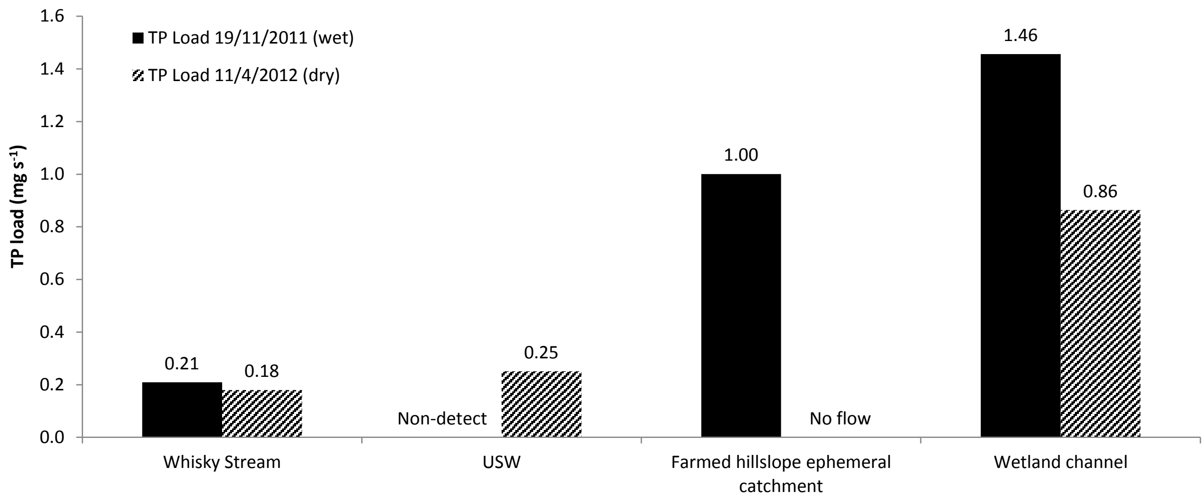

Figure 5-9, Instantaneous TP loads for 19/11/2011 and 11/4/2012

5.3 Additional sources of nitrogen into Lake Clearwater

Concentration was higher in the lake outlet than in the lake inlet (wetland channel). The wetland channel is the only surface water inlet to the lake downstream of farmed land and annual load from the wetland channel accounts for only 40% of the load at LS1, the lake's only surface water outlet. Surface water TN export from Lake Clearwater (2518 kg year-1) was estimated to be 83% greater than total measured loads into the lake (1375 kg year-1). Unaccounted for nitrogen export from Lake Clearwater was estimated to be 611-939 kg year^{-1} for July 2011 – June 2012. Further work to ascertain the cause of high TN concentration in Lake Clearwater would be usefull to better manage water quality in the lake.

Although Lambies Stream is the only surface outlet to Lake Clearwater. Surface outflow from the lake was lower than expected (section 3.5) this could indicate that the lake also has subsurface outflow. However, no investigation of subsurface outflow from the lake was undertaken in this study. If subsurface outflow did occur this would increase the TN export from the lake and the discrepancy between measured TN load into the lake and measured TN export from the lake would be even greater.

Results show that subsurface TN load from the farmed hill slope was comparable to surface water load from the farmed hill slope. However, no estimates were made in this study of potential subsurface load from beneath the wetland into the lake. It is possible a large amount of nitrogen enters the lake below the wetland channel in unmeasured subsurface flow.

It is also possible that sediment resuspension due to wind-induced turbulence released nitrogen into the lake (section 1.3). Strong norwest winds blow along the length of the lake towards LS1. Wind induced mixing could explain part of the variability seen in nutrient concentrations at LS1. In New Zealand shallow lakes wind-induced resuspension typically dominates the internal nutrient flux (Thomas and Schallenberg 2008) between nutrients stored in the benthic sediments and the water column. However, TN concentration has been rising in Lake Clearwater over the monitoring period from 2004 – 2012 so high nitrogen concentrations have occurred gradually. If resuspension were occurring, increases would be expected to occur over a shorter period.

While this study accounts for TN load from farming and natural land, these may not be the only important sources of TN load into Lake Clearwater. Subsurface leaching from septic systems in the bach community between Lake Camp and Lake Clearwater is possible. The surface of Lake Camp is 13 m above the surface of Lake Clearwater. It is possible that water flows out of Lake Camp into Lake Clearwater via a subsurface flow path below the batch community (Figure 5-10) (Personnel communication Adrian Meredith 5/10/2012). If this were the case, any leached nitrogen from septic waste would rapidly flow into Lake Clearwater.

Other, perhaps minor, sources of nitrogen into the lake could include direct input of urine and faeces from large numbers of waterfowl often found on Lake Clearwater. Atmospheric deposition of nutrients, carried from wind erosion of agricultural land on the Canterbury Plains, may also be a source of nitrogen for high country lakes in Canterbury.

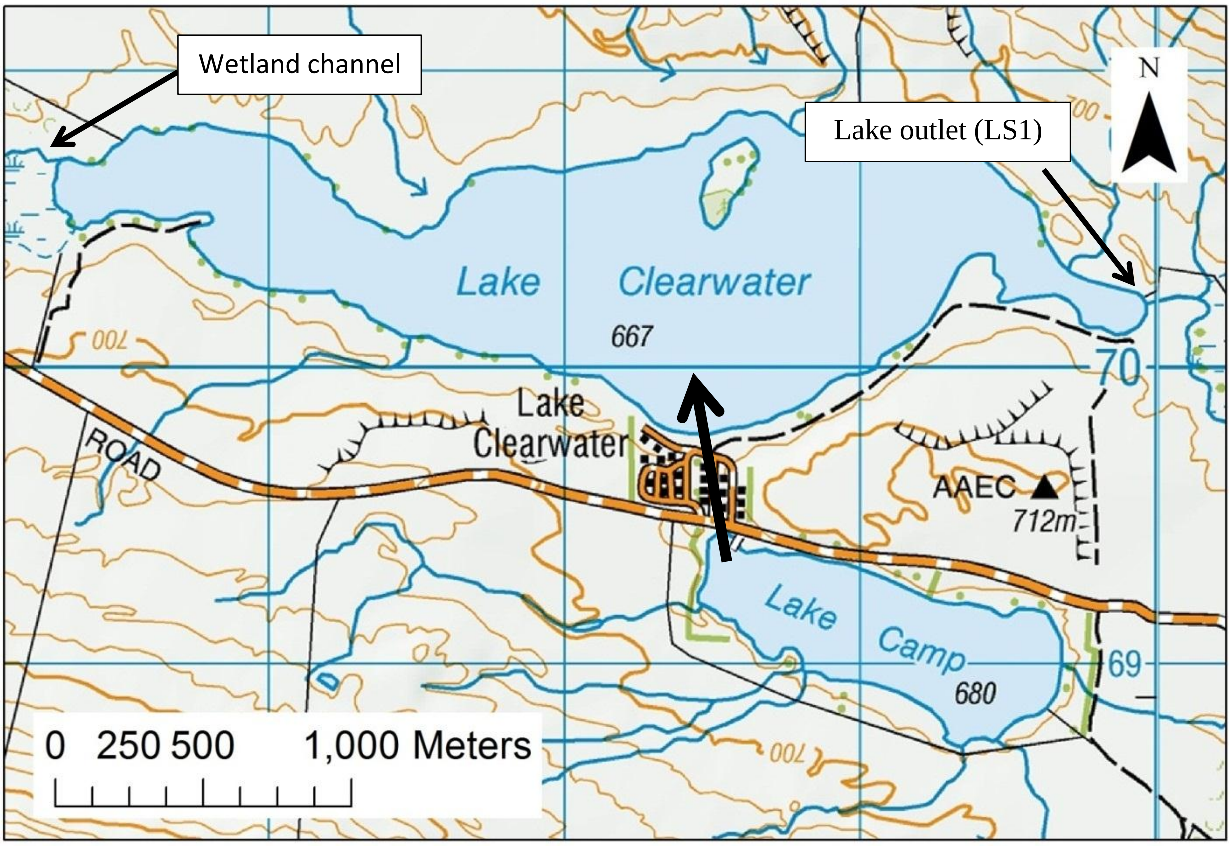

Figure 5-10, Lake Camp and Clearwater. The thick arrow indicates potential subsurface flow

6 CLUES model results

TN and TP loads from the CLUES model are compared with measured loads from key sub catchments in Figure 6-1 and Figure 6-2. Loads from the default model inputs are shown as well as loads using the current land use as an input.

6.1 TN load results

TN loads from the default input were 1.5 to 3 times higher than measured loads. Farmland area in the catchment was overestimated in the model's default land use layer (Figure 2-19). The default land use input layer was predominantly hill country sheep and beef farming over the valley floor in the catchment. However, actual farmed area (4.18 km^2) was only 28% of farmland area in the default CLUES land use input layer. The default CLUES land use layer may have better reflected past land use in the catchment. Before tenure review in 2007, more land area in the Lake Clearwater catchment was used for low-intensity sheep grazing. The overestimate of farmed area in the models input layer was likely to be the primary reason that the CLUES model over predicts TN Loads.

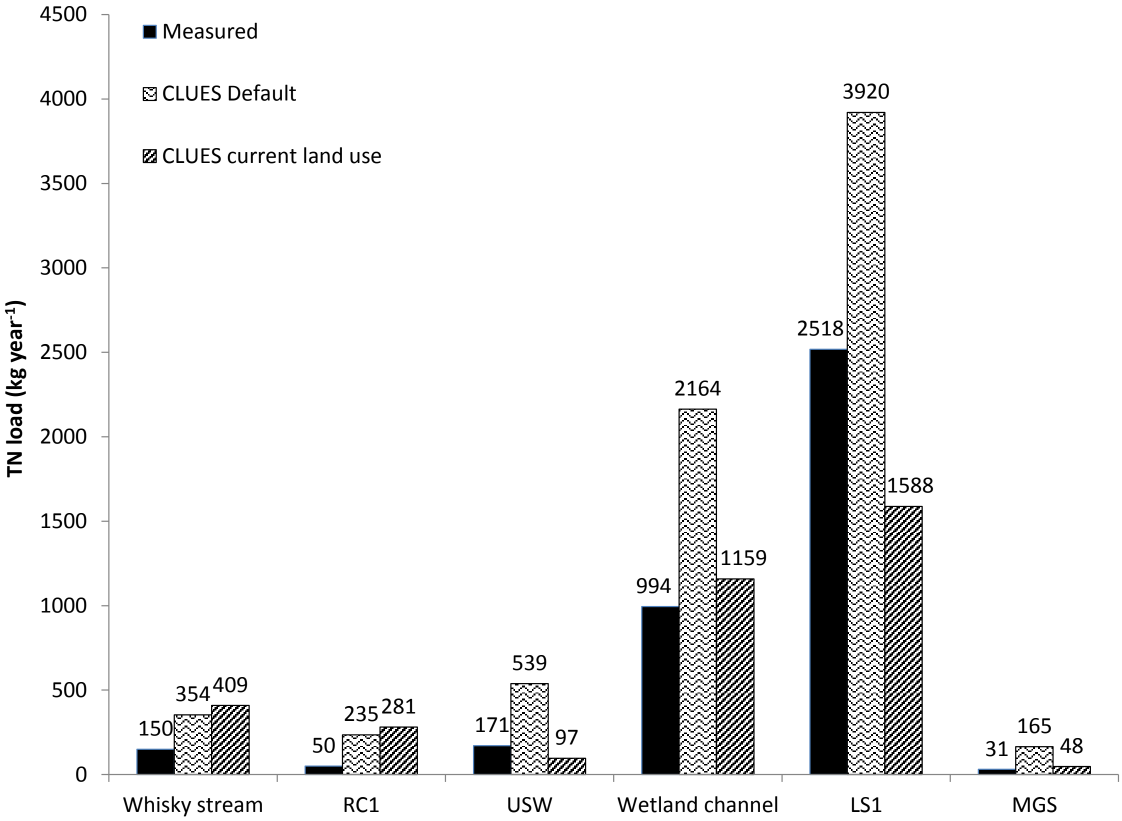

Figure 6-1, Measured and CLUES model predicted TN loadings from key sub catchments

TN load estimates for natural tussock grassland catchments at USW and MGS were reasonable using the current land use layer as an input. The CLUES model load was 35% higher than measured load at MGS. Measured load at MGS was a more reliable load estimate than the estimate at USW because the annual flow was measured directly.

The input scenario using the current land use layer gave predicted TN loads close to those given by the default layer input for surface water runoff from the farmed hillslope (Whisky Stream and RC1). This was expected because land use for these catchments was similar for both input layers. Both inputs give large over estimates compared to measured surface water load for these catchments. The CLUES model assumes that all nutrient load from each catchment exits in surface water at the catchment outlet. This is a reasonable assumption for larger catchments. However, streams in small catchments, such as Whisky Stream and RC1, may not contain all nutrient runoff originating from the land area within that catchment. Nutrient load from shallow subsurface lateral flow is expected to reach surface waterways downstream of the Whisky Stream catchment outlet in the wetland channel. The CLUES model does not include the subsurface load from the farmed hillslope. It assumes all nutrient loads into the wetland are from surface waterways, but the over prediction of loads in Whisky Stream and RC1 may not be important as the total load from the farmed land was predicted reasonably well. The load predicted by CLUES for the wetland channel, using the current land use input layer, was only 17% higher than the measured load. These results indicate that the model gives reasonable estimates of surface water TN loads for high country catchments when land use inputs are corrected to reflect actual land use. However, the loadings are likely to be overestimated in surface water for small catchments if shallow subsurface runoff carries a considerable proportion of total nutrient load. A model with a subsurface return flow component, such as SWAT (Neitsch et al. 2011), could be a useful tool for quantifying the impact of land use in this type of catchment.

The predicted load estimates from the current land use input for the lake outlet (LS1) was 37% lower than the measured load. However, farming was not expected to be the only source of loading to Lake Clearwater (section 5.3). Estimates of TN load from other unmeasured sources (611-939 kg year^{-1}) are made in section 5.1. With these additional loads added to the predicted load at LS1, the predicted load was only 0-13% less than the measured load.

6.2 TP load results

TP loads predicted by the CLUES model are compared with measured load in Figure 6-2. TP load was greatly overestimated by both the default and current land use input layers. This was due to an over estimate of phosphorus load from unfarmed land (tussock grassland) by the SPARROW component of the CLUES model. Sediment load is high in many parts of the Canterbury high country and high sediment estimates caused SPARROW, and therefore CLUES, to predict high TP load for natural catchments. This was not realistic for the Lake Clearwater catchment as TSS was typically below the detection limit (3 g m^{-3}) (section 4.2.5). With the sediment term set to zero, CLUES predictions of TP load from natural catchments were greatly reduced but still larger than measured loads. To further improve agreement with measured loads, the primary source coefficient for SPARROW predictions of TP load from unfarmed land was also adjusted. TP load results from the model run with adjusted source coefficients are also shown in Figure 6-2.

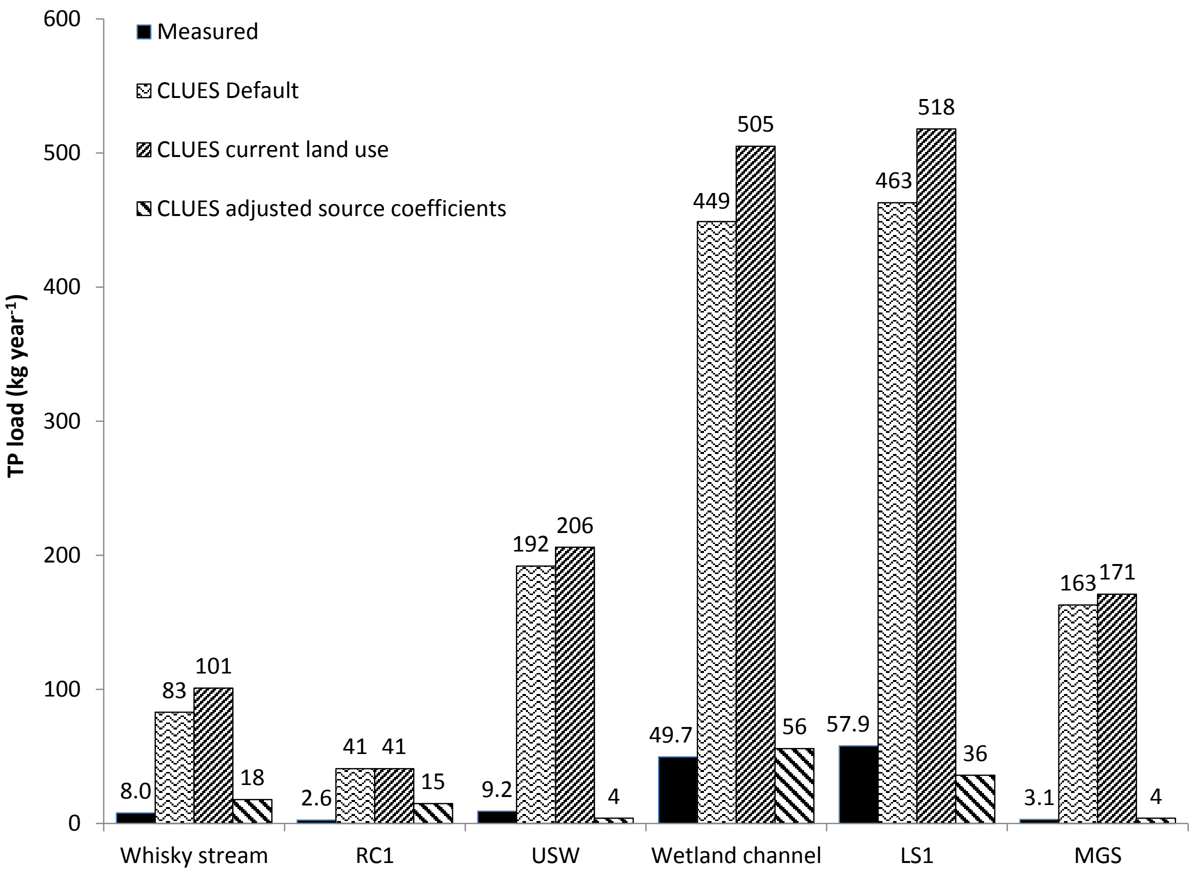

Figure 6-2, Measured and CLUES model predicted TP load from key sub catchments

Once source coefficients were adjusted in SPARROW, the pattern of predicted TP loads was similar to TN loads. Predicted TP load was in reasonable agreement with measured load at MGS. This close agreement was a result of fitting the model to measured natural TP load by changing the source coefficients. It does not infer that the model is capable of predicting TP load well in natural high country catchments. TP load in surface water runoff from the farmed hillslope was over predicted by 477% in RC1 and 125% in Whisky Stream. However, load in the wetland channel was only over predicted by 13%. This was likely to be due to TP load from subsurface lateral flow as described for TN load (section 6.1).

Predicted TP load at LS1 was 38% lower than measured load. This could be due to under estimation of natural TP load entering the lake, in either surface water or subsurface water. It is also possible that attenuation in Lake Clearwater was overestimated by the CLUES model. The CLUES model attempts to predict attenuation processes in lakes and attenuation in Lake Clearwater may have lower attenuation compared to lakes used in the nationwide calibration of the CLUES model.

Predicted TN stream yields from SPARROW in the Waikato basin were typically within 10-15 % of the measured values at monitoring sites. Predicted yields for TP were typically within 20-30 % (Alexander et al. 2002). As discussed above, much greater discrepancies between CLUES predictions and measured loads was seen in the Lake Clearwater catchment.

7 Conclusions and recommendations

Annual flow in all monitored streams ranged from 88 to 223 mm year^{-1}. Subsurface lateral flow from the farmed hillslope into the wetland was estimated at 79 to 146 mm year^{-1}. Annual surface water outflow from Lake Clearwater at Lambies Stream was lower than expected (88 mm year^{-1}), which may indicate unmeasured subsurface outflow and high evaporation (estimated at 29 mm year^{-1} over the entire catchment) from the lake. Streamflow and wetland water levels in winter and spring were much higher than other seasons, especially ephemeral flow, despite similar rainfall across the year. As a result, a high proportion of nutrient load occurred in winter and spring.

Two unimpacted sites (MGS and USW) were sampled to determine un-impacted background nutrient concentrations in perennial streams. Concentrations ranged from 0.1 to 0.17 g m^{-3} for TN and 0.004 to 0.047 g m^{-3} for TP. Nutrient yields for unfarmed land in the Lake Clearwater catchment were found to be low at 0.0837-0.26 kg ha^{-1} year^{-1} for TN and 0.0085-0.014 kg ha^{-1} year^{-1} for TP. Nutrient concentrations were comparable to other upland rivers in Canterbury with natural catchments.

TN concentrations were highest (0.28-2.2 g m^{-3}) in ephemeral streams draining farmland and ephemeral runoff accounted for 35% of the TN load from the farmed hillslope. TP concentrations were also highest (0.013-0.49 g m^{-3}) in ephemeral streams draining the farmland and ephemeral flow was estimated to contribute 41% of TP load from the farmed hillslope. Further surface flow monitoring of ephemeral catchments from the farmland would greatly improve estimates of ephemeral surface runoff and nutrient load. High flow events may carry a large proportion of total nutrient load in ephemeral runoff. Multiple measurements of nutrient concentration during high flow events would improve annual and event load estimates and understanding of nutrient transport from farmland into waterways. Measures to reduce erosion and stock access in ephemeral waterways during wet conditions may help lower phosphorus loads from farmland.

TN concentrations (0.1-0.28 g m^{-3}) in the only perennial stream draining farmland (Whisky Stream) were much lower than ephemeral runoff. Perennial surface runoff was estimated to account for 13% of TN load from the farmed hill slope. Total and dissolved reactive phosphorus concentrations were also much lower than ephemeral runoff and were generally below appropriate water quality guidelines. The median TP concentration in Whisky Stream (0.009 g m^{-3}) was no greater than median concentrations for streams with natural catchments and Whisky Stream only contributed approximately 14% of TP load from the farmed hillslope. However, concentration increased, up to 0.047 g m^{-3}, during some high flow events.

TN concentrations (0.28-0.78 g m^{-3}) in subsurface flow were typically above the ANZECC guidelines and concentrations in perennial surface runoff from the farmed hillslope. Subsurface TN load (236-443 kg year^{-1}) represented approximately 52% of total load from the farmed hillslope. On average, nitrate accounted for 11% of TN in surface water, but in subsurface seeps it accounted for 74% of TN. The median nitrate concentration in the seeps (0.19-0.29 g m^{-3}) was 15-125 times higher than in surface waterways (0.004-0.034 g m^{-3}). The median TP concentration (0.014 g m^{-3}) was also elevated, above natural concentrations, in subsurface runoff but not to the same degree as nitrate.

Downstream from the subsurface return flow, median TP concentrations in the wetland (0.013 g m^{-3}) and the lake outlet (0.013 g m^{-3}) were similar to the subsurface runoff. Subsurface TP load (10-16 kg $year^{-1}$) represented approximately 45% of total load from the farmed hillslope. Subsurface runoff transports a large proportion of nutrient load into the wetland. Direct investigation of groundwater level, flow and concentration via boreholes or tracer tests could provide insight into subsurface flow between the farmland and the wetland channel and flow under the wetland itself.

The median TN concentration in the wetland channel (0.22 gm^{-3}) was higher than all perennial surface water tributaries flowing into the wetland. Nitrate transported by subsurface runoff was thought to account for increasing TN concentration in the portion of wetland channel that runs along the base of the farmed hillslope. TN load from farmland into the wetland was estimated at 656 kg $year^{-1}$. This equated to a TN yield from the farmland of 1.96-2.94 kg ha^{-1} $year^{-1}$. This is low compared to published TN yields for lowland pastoral land use in New Zealand (Cooper and Thomsen 1988; Quinn and Stroud 2002) and was comparable to the lowest yield (2.8 kg ha^{-1} $year^{-1}$) found for New Zealand low intensity pastoral agriculture in Elliott and Sorrell (2002). The Proposed Canterbury Land and Water Regional Plan (Environment Canterbury 2012) has set a preliminary limit of 20 kg ha^{-1} $year^{-1}$ of nitrogen yield from farmland within the catchments of sensitive lakes, such as Lake Clearwater. Results indicate that farmland nitrogen losses in the Lake Clearwater catchment are not likely to reach this limit if current land use practices continue. However, TN concentrations in farmland ephemeral streams, subsurface seeps, the wetland channel and the lake are typically above natural levels and the ANZECC guideline, indicating diffuse nutrient pollution may be having deleterious impacts within the catchment. Elevated nitrogen concentrations may be contributing to observed changes in the wetland vegetation and the rising trophic level of Lake Clearwater. Further work is needed to assess existing or potential effects of elevated nitrogen levels on the native wetland ecological communities. Median TP concentration in the wetland was 0.013 g m^{-3}. Although this was higher than the median concentrations in streams draining natural land, concentrations were still well below the ANZECC guidelines and within measured ranges for natural upland streams in Canterbury. TP load from farmland into the wetland was estimated at 29 kg $year^{-1}$. This equated to a TP yield from the farmland of 0.093-0.123 kg ha^{-1} $year^{-1}$. As with TN, this is very low compared to published TP yields for lowland pastoral land use (Cooper and Thomsen 1988; Quinn and Stroud 2002). TP yield was similar to the minimum value found for New Zealand native catchments (0.12 kg ha^{-1} $year^{-1}$), but approximately a third of the minimum value (0.3 kg ha^{-1} $year^{-1}$) found for low intensity pastoral agriculture in Elliott and Sorrell (2002). Low nutrient yields may reflect the low intensity of the pastoral land use and rapid attenuation of phosphorus in waterways rather than limited nutrient loss from soil into waterways.

Nitrogen has steadily increased in the lake from 2004 and nitrogen concentration passed the eutrophic threshold in 2007. For 2011 and 2012 the median TN concentration in the lake outlet (0.565 g m-3) was 2.6 times higher than in the only lake inlet downstream of farmland (0.22 g m-3). From July 2011 until June 2012, surface water TN export from Lake Clearwater (2518 kg $year^{-1}$) was 83% greater than total estimated load into the lake (1375 kg year-1). Unaccounted for TN export from Lake Clearwater was estimated to be 611-939 kg $year^{-1}$ for July 2011 – June 2012, indicating the lake was a net source of nitrogen. Diffuse TN loads from farmland and natural land may not be the only important sources of TN load into Lake Clearwater. Additional sources of nitrogen into Lake

Clearwater could include unmeasured subsurface load from beneath the main wetland channel or nitrogen leached from septic systems of the bach community. Investigation of groundwater nutrient concentrations and flow beneath and the wetland channel would be useful to address uncertainty regarding the total nutrient load from farmland into Lake Clearwater. Sampling from Lake Clearwater near the wetland outlet and near the bach community, as well as at the lake outlet, may help identify the origin of the high nitrogen concentration in the lake. Investigation of nutrient concentrations in groundwater or return flow seeps down gradient of the batch community would also be useful to identify any potential nitrogen load from septic systems into the lake. The annual (2011-2012) estimated TP export from Lake Clearwater of 58 kg year^{-1} was 24% less than total estimated loads into the lake (76 kg year^{-1}). This indicates attenuation of TP load within the lake. The TN to TP mass ratio in the lake (49:1 by mass) suggests that the productivity of the lake is phosphorus limited. The phosphorus concentration in the lake has tripled from 2004 to 2012 and was approaching the eutrophic threshold (Burns et al. 2000). Increased phosphorus concentration in the lake could lead to increases in phytoplankton and other undesirable algae. Further investigation of nutrient limitation in the lake could be useful to focus short-term efforts to limit productivity in Lake Clearwater.

The CLUES model was used to predict TN and TP loads in waterways within the Lake Clearwater catchment and predicted loads were compared to measured loads. For default inputs, TN loads were over predicted by 1.5 to 3 times and TP loads were over predicted by up to 9 times. After modifying the land use input layer to reflect current land use, predicted TN load was only 17% higher than the measured load in the wetland channel and 35% higher than the measured load at MGS. CLUES overestimated TN load in surface runoff from the farmed hillslope. A likely reason for this was that the model assumes all nutrient load from each sub catchment is transported out of the catchment in surface water runoff. This study has shown that considerable nutrient load enters the wetland directly via subsurface flow. Results in this study indicate that the TN loads predicted by the CLUES model are reasonable in catchments similar to the Lake Clearwater catchment provided the land use information is accurate, important TN sources are accounted for and most nutrient loss exits the catchment in surface water. The CLUES model was less able to predict TP loads in this catchment. TP load was greatly overestimated by both the default and current land use input layers. This was primarily due to high estimates of sediment load causing high estimates of phosphorus load in unfarmed catchments. Clues estimates of TP load in highcountry catchments such as the Lake Clearwater catchment should be treated with caution.

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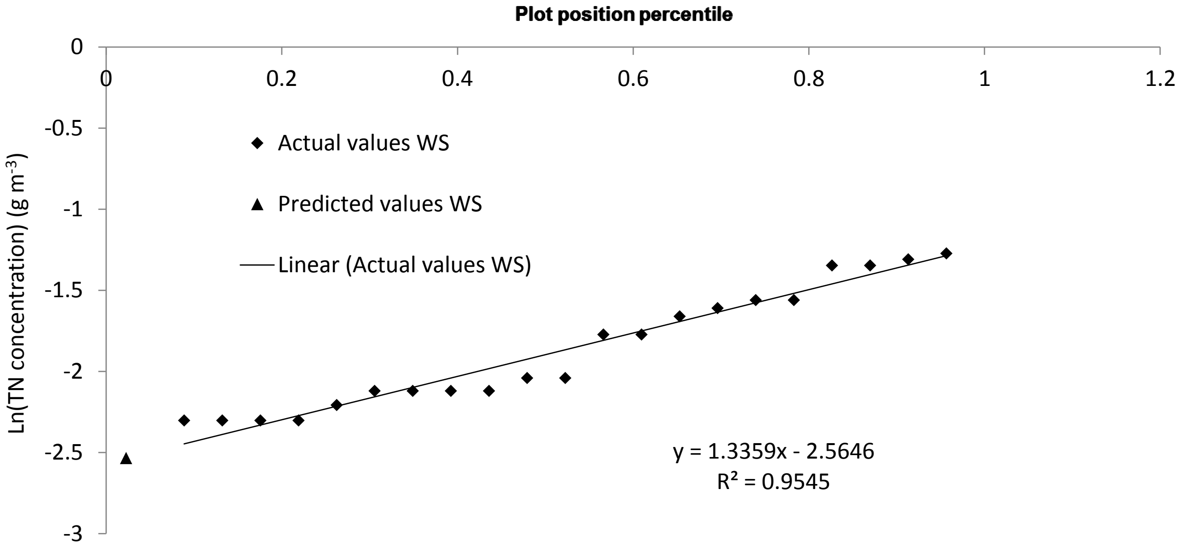
Appendix A . Hill Laboratory analysis methods

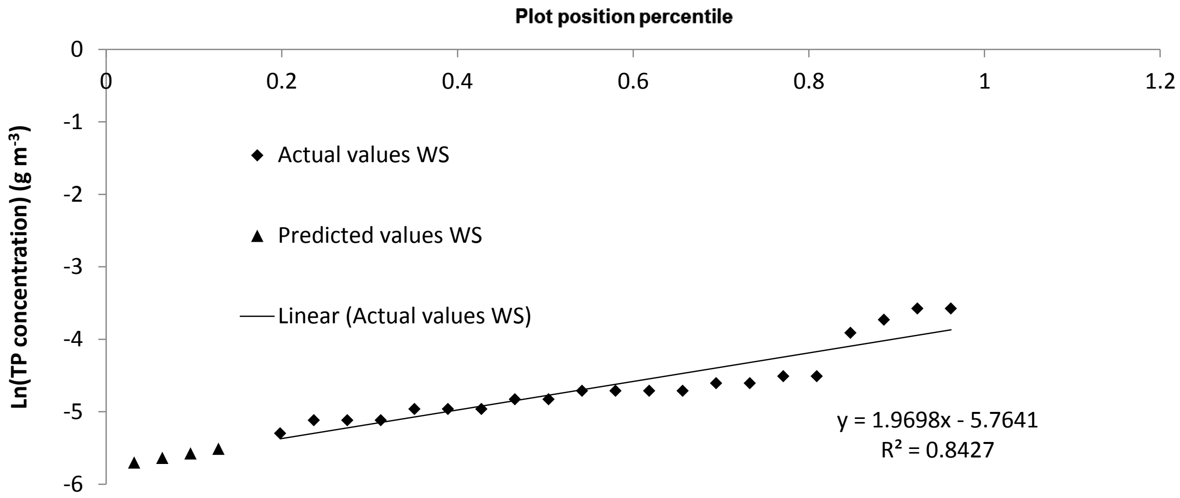
The table below briefly presents analysis methods used by Hill Laboratory for the analytes in this study.

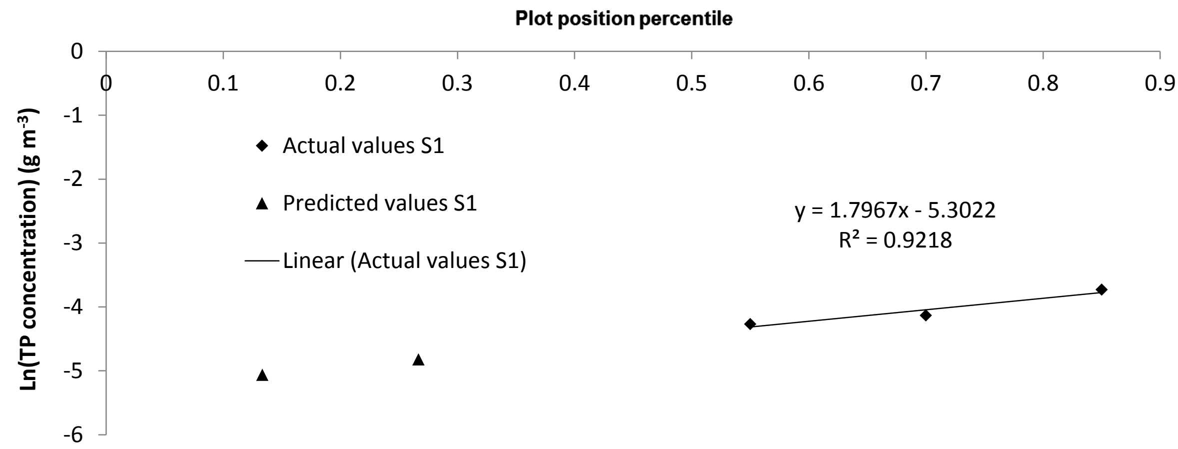
Test	Parameter	Method description	Detection limit
Filtration, Unpreserved	All	Sample filtration through 0.45µm membrane filter.	-
Total Kjeldahl Digestion	TKN	Sulphuric acid digestion with copper sulphate catalyst.	-
Total Phosphorus Digestion	TP	Acid persulphate digestion.	-
Total Suspended Solids	TSS	Filtration using Whatman 934 AH, Advantec GC-50 or equivalent filters (nominal pore size 1.2 - 1.5µm), gravimetric determination. APHA 2540 D 21st ed. 2005.	3 g m^{-3}
Total Nitrogen	TN	Calculation: TKN + Nitrate-N + Nitrite-N.	0.05 g m^{-3}
Total Ammoniacal-N	NH_4-N	Filtered sample. Phenol/hypochlorite colorimetry. Discrete Analyser. (NH4-N = NH4+-N + NH3-N). APHA 4500-NH3 F 21st ed. 2005.	0.010 g m^{-3}
Nitrate-N + Nitrite-N	NO_3 + NO_2-	Total oxidised nitrogen. Automated cadmium reduction, flow injection analyser. APHA 4500-NO3- I 21st ed. 2005.	0.002 g m^{-3}
Total Kjeldahl Nitrogen (TKN)	TKN	Total Kjeldahl digestion, phenol/hypochlorite colorimetry. Discrete Analyser. APHA 4500-Norg C. 4500 NH3 F 21st ed. 2005.	0.10 g m^{-3}
Dissolved Reactive Phosphorus	DRP	Filtered sample. Molybdenum blue colorimetry. Discrete Analyser. APHA 4500-P E) 21st ed. 2005.	0.004 g m^{-3}
Total Phosphorus	TP	Total phosphorus digestion, ascorbic acid colorimetry. Discrete Analyser. APHA 4500-P E 21st ed. 2005.	0.004 g m^{-3}

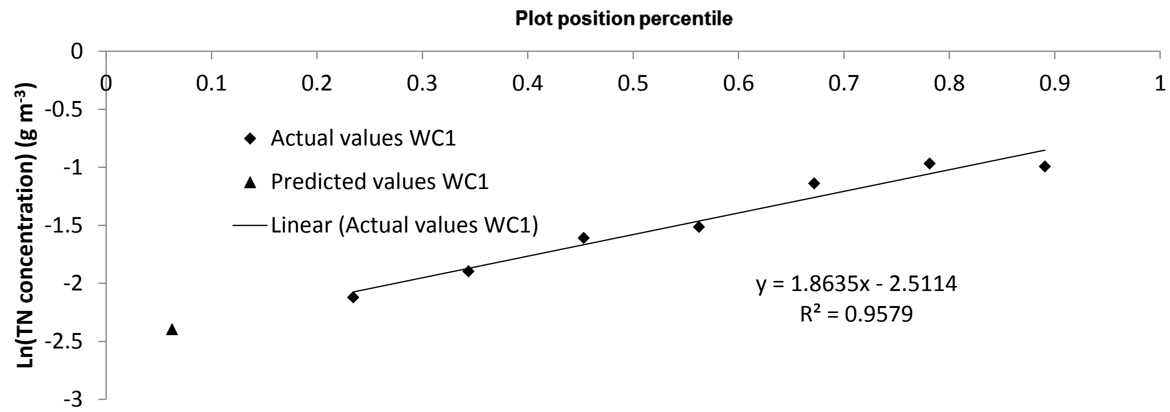
Appendix B . Prediction of non-detect TN and TP concentrations using robust Regression on Order Statistics (ROS)

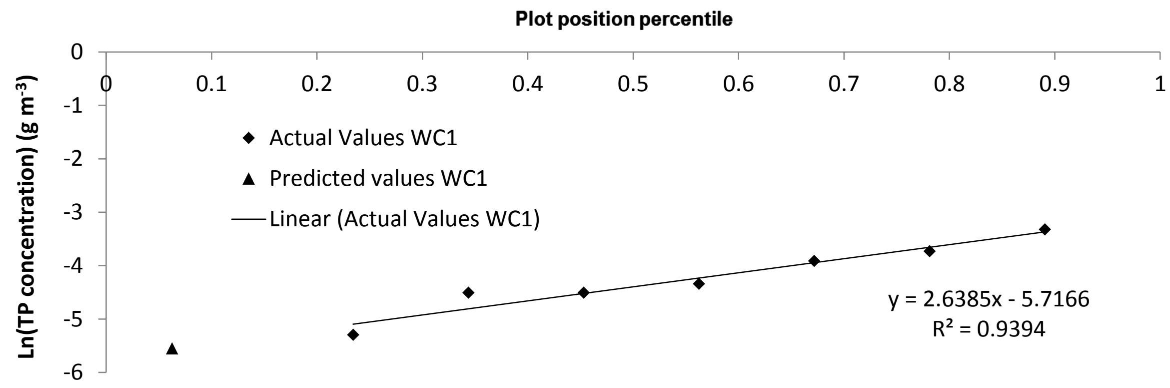
The following scatter plots show measured values and values predicted by ROS for TN and TP at six sites: Whisky Stream (WS), Seep One (S1) (TP only), Wetland Channel One (WC1), Upstream Wetland (USW) and Mt Guy Stream (MGS).

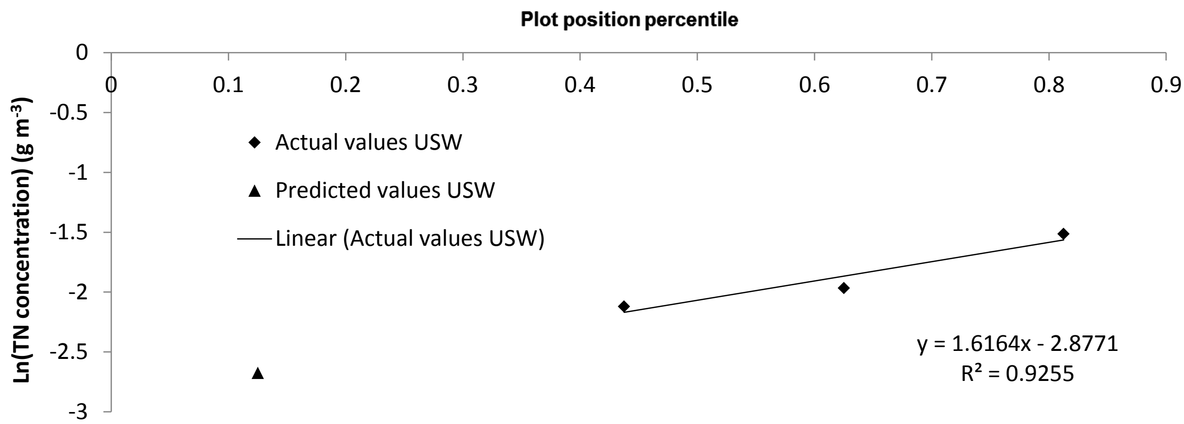


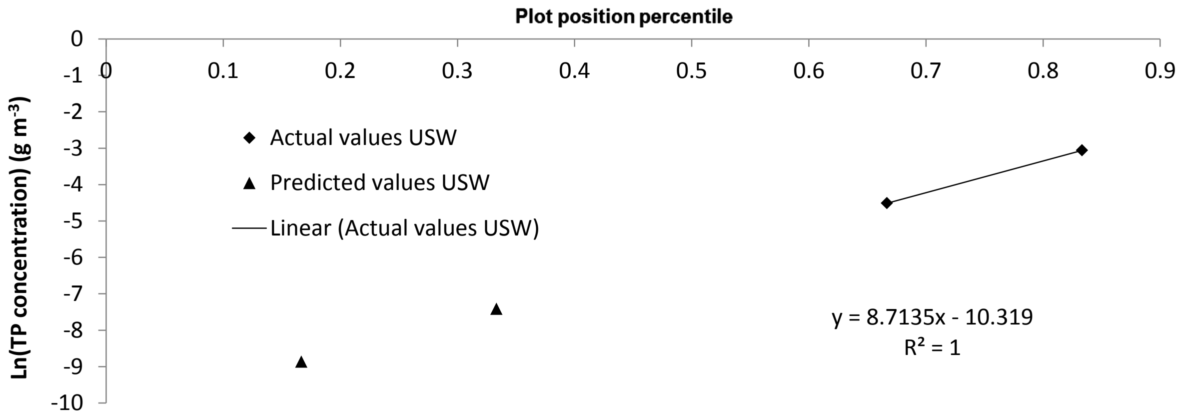


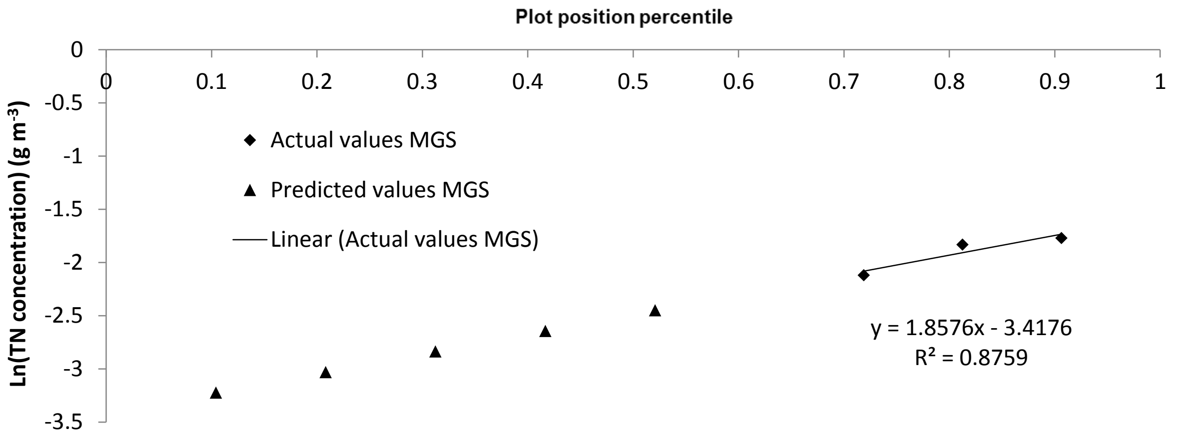

Plot position percentile
Ln(TP concentration) (g m-3)
Actual values S1
Predicted values S1
Linear (Actual values S1)
y = 1.7967x - 5.3022
R² = 0.9218

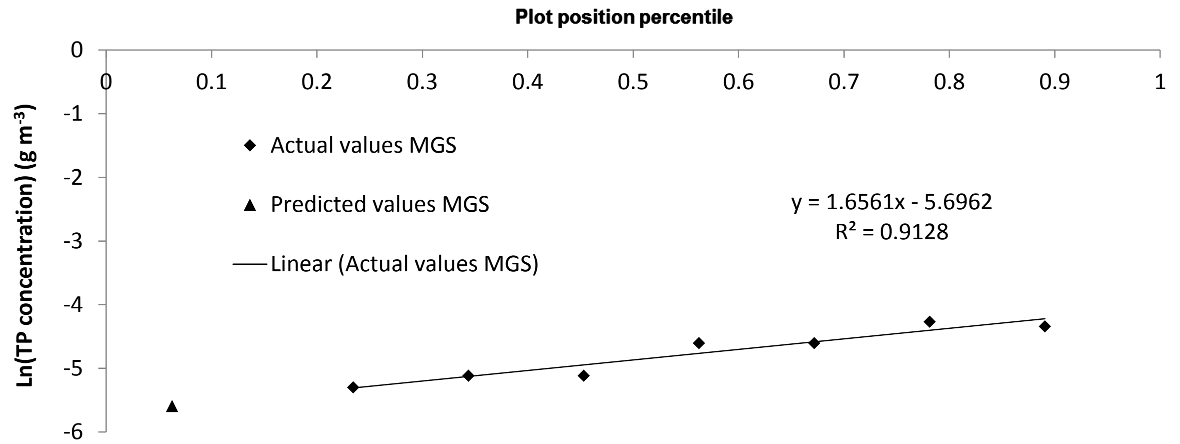

Plot position percentile
Ln(TN concentration) (g m-3)
Actual values WC1
Predicted values WC1
Linear (Actual values WC1)
y = 1.8635x - 2.5114
R² = 0.9579


Plot position percentile
Ln(TP concentration) (g m-3)
Actual Values WC1
Predicted values WC1
Linear (Actual Values WC1)
y = 2.6385x - 5.7166
R² = 0.9394


Plot position percentile
Ln(TN concentration) (g m-3)
Actual values USW
Predicted values USW
Linear (Actual values USW)
y = 1.6164x - 2.8771
R² = 0.9255


Plot position percentile
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Ln(TP concentration) (g m-3)
Actual values USW
Predicted values USW
Linear (Actual values USW)
y = 8.7135x - 10.319
R² = 1


Plot position percentile
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Ln(TN concentration) (g m-3)
Actual values MGS
Predicted values MGS
Linear (Actual values MGS)
y = 1.8576x - 3.4176
R² = 0.8759


Plot position percentile
0
-1
-2
-3
-4
-5
-6
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Ln(TP concentration) (g m-3)
Actual values MGS
Predicted values MGS
Linear (Actual values MGS)
y = 1.6561x - 5.6962
R² = 0.9128

Appendix C . Nutrient concentration results

All TSS and nutrient concentration results are shown. Summary statistics are shown below, followed by individual concentrations for each sampling event. Redder colours indicate higher values and colours towards green indicate lower values compared to all other samples. Site abbreviations at the top of columns correspond with sites in Figure 2-13 and Figure 2-14. Standard deviation (SD) and the coefficient of variation (COV) are abbreviated. Analyte abbreviations are defined in Section 2.5.4. N/A indicates no sample was taken at this sampling event.

		WS1	WS2	WS3	RC1	RC2	RC3	S1	S4	S5	USW	WC1	WC2	WC3	LS1	MGS
TSS	Min	0	3	6	5	0	30	3	200	0	3	3	0	0	3	0
	Max	0	3	6	144	0	81	7	200	0	8	8	0	0	6	0
	Mean	N/A	N/A	N/A	35	N/A	56	5	N/A	N/A	6	5	N/A	N/A	5	N/A
	Median	N/A	N/A	N/A	7	N/A	56	6	N/A	N/A	6	4	N/A	N/A	4	N/A
	SD	N/A	N/A	N/A	60.961	N/A	36.062	2.082	N/A	N/A	3.536	2.646	N/A	N/A	1.342	N/A
	COV	N/A	N/A	N/A	1.732	N/A	0.650	0.390	N/A	N/A	0.643	0.529	N/A	N/A	0.292	N/A
TN	Min	0.100	0.100	0.100	0.480	0.410	0.280	0.300	0.280	0.310	0.120	0.120	0.170	0.210	0.350	0.120
	Max	0.260	0.270	0.280	1.650	0.540	2.200	0.780	0.310	0.320	0.220	0.380	0.490	0.490	1.010	0.170
	Mean	0.169	0.159	0.171	0.812	0.463	1.253	0.424	0.295	0.315	0.160	0.251	0.293	0.343	0.579	0.150
	Median	0.120	0.150	0.160	0.600	0.440	1.280	0.340	0.295	0.315	0.140	0.220	0.260	0.330	0.565	0.160
	SD	0.072	0.054	0.069	0.483	0.068	0.960	0.200	0.021	0.007	0.053	0.105	0.116	0.140	0.211	0.026
	COV	0.428	0.341	0.405	0.594	0.147	0.766	0.472	0.072	0.022	0.331	0.419	0.396	0.409	0.364	0.176
NH_4	Min	0.012	0.024	0.019	0.012	0.000	0.012	0.000	0.000	0.000	0.034	0.015	0.020	0.000	0.017	0.000
	Max	0.012	0.034	0.019	0.114	0.000	0.045	0.000	0.000	0.000	0.034	0.015	0.035	0.000	0.034	0.000
	Mean	N/A	0.028	N/A	0.063	N/A	0.029	N/A	N/A	N/A	**N/A**	N/A	0.028	N/A	0.026	N/A
	Median	N/A	0.026	N/A	0.063	N/A	0.029	N/A	N/A	N/A	N/A	N/A	0.028	N/A	0.026	N/A
	SD	N/A	0.005	N/A	0.072	N/A	0.023	N/A	N/A	N/A	N/A	N/A	0.011	N/A	0.012	N/A
	COV	N/A	0.189	N/A	1.145	N/A	0.819	N/A	N/A	N/A	N/A	N/A	0.386	N/A	0.471	N/A
NNN	Min	0.008	0.002	0.003	0.017	0.002	0.016	0.250	0.187	0.230	0.007	0.003	0.003	0.004	0.003	0.013
	Max	0.019	0.024	0.018	0.520	0.023	0.030	0.290	0.191	0.250	0.008	0.021	0.022	0.014	0.009	0.034
	Mean	0.013	0.018	0.009	0.196	0.003	0.024	N/A	N/A	N/A	0.034	0.009	0.014	0.009	0.014	0.014
	Median	0.016	0.005	0.004	0.052	0.004	0.026	0.270	0.189	0.240	0.008	0.006	0.004	0.010	0.004	0.014

	SD	0.005	0.009	0.007	0.281	0.012	0.007	0.018	0.003	0.014	0.001	0.008	0.008	0.005	0.003	0.010
	COV	0.390	0.535	0.786	1.430	3.863	0.300	N/A	N/A	N/A	0.021	0.840	0.579	0.539	0.196	0.747
TKN	Min	0.100	0.100	0.100	0.420	0.400	0.260	0.110	0.120	0.000	0.120	0.110	0.150	0.200	0.340	0.160
	Max	0.260	0.260	0.270	1.130	0.520	2.200	0.510	0.120	0.000	0.220	0.370	0.420	0.480	1.010	0.160
	Mean	0.172	0.153	0.168	0.694	0.450	1.237	0.310	0.120	N/A	0.160	0.227	0.258	0.337	0.574	0.160
	Median	0.160	0.120	0.160	0.600	0.430	1.250	0.310	0.120	N/A	0.140	0.220	0.210	0.330	0.565	0.160
	SD	0.073	0.054	0.067	0.278	0.062	0.970	0.283	N/A	N/A	0.053	0.091	0.108	0.140	0.212	0.000
	COV	0.426	0.351	0.398	0.401	0.139	0.784	0.912	N/A	N/A	0.331	0.402	0.417	0.416	0.370	0.000
DRP	Min	0.010	0.005	0.005	0.013	0.025	0.005	0.000	0.000	0.013	0.000	0.011	0.007	0.008	0.000	0.005
	Max	0.010	0.005	0.009	0.013	0.025	0.026	0.000	0.000	0.013	0.000	0.011	0.007	0.008	0.000	0.005
	Mean	N/A	N/A	0.007	N/A	N/A	0.016	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	Median	N/A	N/A	0.007	N/A	N/A	0.016	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	SD	N/A	N/A	0.003	N/A	N/A	0.015	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	COV	N/A	N/A	0.404	N/A	N/A	0.958	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
TP	Min	0.005	0.006	0.006	0.024	0.017	0.013	0.014	0.006	0.010	0.011	0.005	0.008	0.011	0.008	0.001
	Max	0.028	0.020	0.028	0.490	0.044	0.189	0.024	0.016	0.014	0.047	0.036	0.016	0.016	0.020	0.013
	Mean	0.011	0.010	0.014	0.127	0.027	0.093	0.018	0.011	0.012	0.029	0.017	0.012	0.014	0.014	0.007
	Median	0.009	0.008	0.010	0.031	0.019	0.076	0.016	0.011	0.012	0.029	0.013	0.013	0.014	0.013	0.006
	SD	0.008	0.005	0.009	0.203	0.015	0.089	0.005	0.007	0.003	0.025	0.010	0.003	0.003	0.004	0.004
	COV	0.747	0.481	0.644	1.599	0.564	0.962	0.294	0.643	0.236	0.878	0.608	0.221	0.184	0.297	0.529

Test	Date	WS1	WS2	WS3	RC1	RC2	RC3	S1	S2	S4	S5	USW	WC1	WC2	Old Inlet	LS1	MGS
Total Suspended Solids - g/m^3	**2010-05-25**	< 3	3	6	144	NS	81	NS	NS	NS	NS	NS	8	NS	< 3	4	< 3
	2010-07-19	< 3	< 3	< 3	15	NS	< 3	NS	NS	NS	NS	NS	< 3	NS	< 3	< 3	< 3
	2010-08-09	< 3	< 3	< 3	7	< 3	30	NS	NS	NS	NS	NS	< 3	NS	< 3	3	< 3
	2011-09-01	< 3	< 3	< 3	5	NS	NS	NS	NS	NS	NS	NS	< 3	< 3	NS	< 3	< 3
	2011-11-19	< 3	< 3	< 3	5	NS	NS	NS	NS	NS	NS	3	4	< 3	NS	< 3	< 3
Stormflow Composite	**2011-11-21**	NS	< 3	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	2011-11-22	NS	< 3	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	2012-03-15	< 3	3	< 3	NS	NS	NS	3	NS	NS	NS	8	< 3	< 3	NS	6	< 3
	2012-04-11	< 3	< 3	< 3	NS	NS	NS	6	NS	NS	NS	< 3	< 3	< 3	NS	4	< 3
	2012-05-01	NS	NS	NS	NS	NS	NS	7	48.000	NS	NS	NS	NS	NS	NS	NS	NS
	2012-05-11	NS	NS	NS	NS	NS	NS	< 3	NS	200	< 3	NS	NS	NS	NS	NS	NS
	2012-06-14	< 3	< 3	< 3	NS	< 3	NS	< 3	NS	< 3	< 3	< 3	3	< 3	NS	6	< 3
Total Nitrogen - g/m^3	**2010-05-25**	0.26	NS	0.28	1.65	NS	1.28	NS	NS	NS	NS	NS	0.37	0.49	0.49	0.35	0.17
	2010-07-19	0.1	0.13	0.1	0.48	0.41	0.28	NS	NS	NS	NS	NS	0.15	0.21	0.21	0.35	<0.110
	2010-08-09	0.120	0.110	0.100	0.540	0.440	2.200	NS	NS	NS	NS	NS	<0.110	0.330	0.330	1.010	<0.110
	2011-09-01	0.260	0.210	0.200	0.790	NS	NS	NS	NS	NS	NS	NS	0.380	0.420	NS	0.590	<0.110
	2011-11-19	0.120	0.100	0.120	0.600	NS	NS	NS	NS	NS	NS	0.120	0.320	0.310	NS	0.630	<0.110
Stormflow Composite	**2011-11-21**	NS	0.270	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	2011-11-22	NS	0.170	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	2012-03-15	<0.110	0.120	0.130	NS	NS	NS	0.36	NS	NS	NS	0.220	0.120	0.200	NS	0.490	<0.110
	2012-04-11	0.210	0.170	0.190	NS	NS	NS	0.30	NS	NS	NS	0.140	0.220	0.210	NS	0.540	0.160
	2012-05-01	NS	NS	NS	NS	NS	NS	0.78	0.320	NS	NS	NS	NS	NS	NS	NS	NS
	2012-05-11	NS	NS	NS	NS	NS	NS	0.34	NS	0.310	0.320	NS	NS	NS	NS	NS	NS
	2012-06-14	0.110	0.150	0.250	NS	0.540	NS	0.340	NS	0.280	0.310	<0.110	0.200	0.170	NS	0.670	0.120

Ammoniacal-N - g/m^3	**2010-05-25**	<0.010	<0.010	<0.010	0.114	NS	0.012	NS	NS	NS	NS	NS	<0.010	NS	<0.010	0.017	<0.010
	2010-07-19	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	NS	NS	NS	NS	NS	<0.010	NS	<0.010	<0.010	<0.010
	2010-08-09	<0.010	<0.010	<0.010	<0.010	<0.010	0.045	NS	NS	NS	NS	NS	<0.010	NS	<0.010	<0.010	<0.010
	2011-09-01	<0.010	<0.010	<0.010	0.012	NS	NS	NS	NS	NS	NS	NS	0.015	<0.010	NS	<0.010	<0.010
	2011-11-19	<0.010	<0.010	<0.010	<0.010	NS	NS	NS	NS	NS	NS	NS	<0.010	0.020	NS	NS	NS
Stormflow Composite	**2011-11-21**	NS	<0.010	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	2011-11-22	NS	0.034	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	2012-03-15	0.012	0.026	0.019	NS	NS	NS	<0.010	NS	NS	NS	0.034	<0.010	0.035	NS	0.034	<0.010
	2012-04-11	<0.010	0.024	<0.010	NS	NS	NS	<0.010	NS	NS	NS		<0.010	<0.010	NS		<0.010
	2012-05-01	NS	NS	NS	NS	NS	NS	<0.010	0.013	NS	NS	NS	NS	NS	NS	NS	NS
	2012-05-11	NS	NS	NS	NS	NS	NS	<0.010	NS	<0.010	<0.010	NS	NS	NS	NS	NS	NS
	2012-06-14	<0.010	<0.010	<0.010	NS	<0.010	NS	<0.010	NS	<0.010	<0.010	<0.010	<0.010	<0.010	NS	<0.010	<0.010
Nitrate-N + Nitrite-N - g/m^3	**2010-05-25**	0.019	NS	0.014	0.52	NS	0.03	NS	NS	NS	NS	NS	0.021	NS	0.014	<0.002	0.015
	2010-07-19	0.013	0.002	0.003	0.052	0.004	0.016	NS	NS	NS	NS	NS	<0.002	NS	0.01	0.008	0.013
	2010-08-09	0.008	0.002	0.004	0.017	0.002	0.026	NS	NS	NS	NS	NS	<0.002	NS	0.004	0.009	0.013
	2011-09-01	<0.002	<0.002	<0.002	<0.002	NS	NS	NS	NS	NS	NS	NS	0.003	0.004	NS	<0.002	<0.002
	2011-11-19	<0.002	<0.002	0.004	<0.002	NS	NS	NS	NS	NS	NS	<0.002	0.003	0.003	NS	0.004	<0.002
Stormflow Composite	**2011-11-21**	NS	0.013	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	2011-11-22	NS	<0.002	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	2012-03-15	<0.002	0.005	<0.002	NS	NS	NS	0.25	NS	NS	NS	0.008	0.006	0.007	NS	0.004	<0.002
	2012-04-11	<0.002	<0.002	<0.002	NS	NS	NS	0.25	NS	NS	NS	<0.002	<0.002	0.003	NS	0.003	<0.002
	2012-05-01	NS	NS	NS	NS	NS	NS	0.27	<0.002	NS	NS	NS	NS	NS	NS	NS	NS
	2012-05-11	NS	NS	NS	NS	NS	NS	0.29	NS	0.19	0.25	NS	NS	NS	NS	NS	NS
	2012-06-14	0.018	0.024	0.018	NS	0.023	NS	0.280	NS	0.187	0.230	0.007	0.011	0.022	NS	<0.002	0.034

Kjeldahl Nitrogen (TKN) - g/m^3		**2010-05-25**	0.24	NS	0.27	1.13	NS	1.25	NS	NS	NS	NS	NS	0.23	NS	0.48	0.35	0.16
		2010-07-19	0.1	0.12	0.1	0.42	0.4	0.26	NS	NS	NS	NS	NS	0.15	NS	0.2	0.34	<0.100
		2010-08-09	0.110	0.110	0.100	0.530	0.430	2.200	NS	NS	NS	NS	NS	<0.100	NS	0.330	1.010	<0.100
		2011-09-01	0.260	0.210	0.200	0.790	NS	NS	NS	NS	NS	NS	NS	0.370	0.420	NS	0.590	<0.100
		2011-11-19	0.110	0.100	0.110	0.600	NS	NS	NS	NS	NS	NS	0.120	0.320	0.310	NS	0.620	<0.100
	Stormflow Composite	**2011-11-21**	NS	0.260	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
		2011-11-22	NS	0.170	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
		2012-03-15	<0.100	0.120	0.130	NS	NS	NS	0.11	NS	NS	NS	0.220	0.110	0.200	NS	0.480	<0.100
		2012-04-11	0.210	0.170	0.190	NS	NS	NS	<0.100	NS	NS	NS	0.140	0.220	0.210	NS	0.540	0.160
		2012-05-01	NS	NS	NS	NS	NS	NS	0.51	0.32	NS	NS	NS	NS	NS	NS	NS	NS
		2012-05-11	NS	NS	NS	NS	NS	NS	<0.100	NS	0.120	<0.100	NS	NS	NS	NS	NS	NS
		2012-06-14	<0.100	0.120	0.240	NS	0.520	NS	<0.100	NS	<0.100	<0.100	<0.100	0.190	0.150	NS	0.660	<0.100
Dissolved Reactive Phosphorus - g/m^3		**2010-05-25**	0.01	NS	0.009	0.013	NS	0.026	NS	NS	NS	NS	NS	0.011	NS	0.008	<0.004	0.005
		2010-07-19	<0.004	<0.004	<0.004	<0.004	<0.004	0.005	NS	NS	NS	NS	NS	<0.004	NS	<0.004	<0.004	<0.004
		2010-08-09	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	NS	NS	NS	NS	NS	<0.004	NS	<0.004	<0.004	<0.004
		2011-09-01	<0.004	<0.004	<0.004	<0.004	NS	NS	NS	NS	NS	NS	NS	<0.004	<0.004	NS	<0.004	<0.004
		2011-11-19	<0.004	<0.004	0.005	<0.004	NS	NS	NS	NS	NS	NS	<0.004	<0.004	0.007	NS	<0.004	<0.004
	Stormflow Composite	**2011-11-21**	NS	0.005	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
		2011-11-22	NS	<0.004	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
		2012-03-15	<0.004	<0.004	<0.004	NS	NS	NS	<0.004	NS	NS	NS	<0.004	<0.004	<0.004	NS	<0.004	<0.004
		2012-04-11	<0.004	<0.004	<0.004	NS	NS	NS	<0.004	NS	NS	NS	<0.004	<0.004	<0.004	NS	<0.004	<0.004
		2012-05-01	NS	NS	NS	NS	NS	NS	<0.004	<0.004	NS	NS	NS	NS	NS	NS	NS	NS
		2012-05-11	NS	NS	NS	NS	NS	NS	<0.004	NS	<0.004	0.013	NS	NS	NS	NS	NS	NS
		2012-06-14	<0.004	<0.004	<0.004	NS	0.025	NS	<0.004	NS	<0.004	<0.004	<0.004	<0.004	<0.004	NS	<0.004	<0.004

Total Phosphorus - g/m^3	**2010-05-25**	0.028	NS	0.024	0.49	NS	0.189	NS	NS	NS	NS	NS	0.024	0.014	0.014	0.019	0.013
	2010-07-19	<0.004	<0.004	<0.004	0.064	0.017	0.013	NS	NS	NS	NS	NS	0.005	0.011	0.011	0.012	0.005
	2010-08-09	0.005	<0.004	0.009	0.031	0.019	0.076	NS	NS	NS	NS	NS	<0.004	0.016	0.016	0.012	0.006
	2011-09-01	0.01	0.007	0.006	0.027	NS	NS	NS	NS	NS	NS	NS	0.011	0.013	NS	0.008	0.006
	2011-11-19	0.007	0.008	0.01	0.024	NS	NS	NS	NS	NS	NS	<0.004	0.036	0.013	NS	0.011	<0.004
Stormflow Composite	**2011-11-21**	NS	0.02	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	2011-11-22	NS	0.006	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	2012-03-15	0.006	0.011	0.007	NS	NS	NS	0.016	NS	NS	NS	0.047	0.011	0.009	NS	0.017	0.01
	2012-04-11	0.009	0.009	0.011	NS	NS	NS	0.024	NS	NS	NS	0.011	0.013	0.014	NS	0.014	0.01
	2012-05-01	NS	NS	NS	NS	NS	NS	0.014	0.096	NS	NS	NS	NS	NS	NS	NS	NS
	2012-05-11	NS	NS	NS	NS	NS	NS	<0.004	NS	0.016	0.014	NS	NS	NS	NS	NS	NS
	2012-06-14	0.009	0.008	0.028	NS	0.044	NS	<0.005	NS	0.006	0.01	<0.004	0.02	0.008	NS	0.02	0.0014

Appendix D . *In-situ* water quality tables

Results from *in-situ* measurements are shown. Summary statistics are shown below, followed by individual measurements for each sampling event. Abbreviations and colours are defined in Appendix C.

		WS1	WS2	WS3	RC1	RC2	S1	S2	S4	S5	USW	WC1	WC2	MGS	LS1
Number of samples		8	9	8	5	3	5	1	2	2	4	8	8	8	8
DO	Min	9.75	9.45	9.45	6.35	12.29	8.58	4.5	9	9	9.14	10.5	9.79	10.29	9.64
	Max	14	14	13	13	14	9	5	10	10	13	13	12	12	14
	Mean	12	12	11	10	13	9	5	9	10	11	11	11	11	11
	Median	11	12	11	11	13	9	5	9	10	10	11	12	11	11
	SD	1.467	1.585	1.381	2.629	0.671	0.231	N/A	0.636	0.813	1.913	0.973	0.921	0.772	1.402
	COV	0.125	0.137	0.120	0.263	0.052	0.026	N/A	0.067	0.085	0.178	0.086	0.081	0.068	0.125
pH	Min	6.64	6.88	6.85	6.1	6.46	5.88	5.86	6.21	6.44	6.66	6.29	6.38	6.22	6.22
	Max	8	8	8	7	7	8	6	7	7	8	8	8	8	8
	Mean	7	8	7	7	7	7	6	6	7	7	7	7	7	7
	Median	7	8	7	7	7	7	6	6	7	7	7	7	7	7
	SD	0.584	0.429	0.366	0.569	0.247	0.755	N/A	0.354	0.304	0.503	0.452	0.507	0.562	0.607
	COV	0.079	0.057	0.050	0.085	0.037	0.113	N/A	0.055	0.046	0.070	0.064	0.072	0.079	0.087
Conductance	Min	24.9	25.1	25.1	30.7	39.5	35.6	94	33.5	62	12.5	25	22.2	36.1	35.9
	Max	67	67	66	60	74	57	94	54	63	28	65	69	74	62
	Mean	42	41	41	43	52	48	94	44	63	20	37	35	51	48
	Median	39	38	39	45	42	55	94	44	63	20	32	29	44	45
	SD	14.962	14.259	14.342	10.888	19.309	11.127	N/A	14.566	0.778	6.268	13.976	15.825	15.252	10.188
	COV	0.359	0.350	0.346	0.251	0.371	0.233	N/A	0.333	0.012	0.317	0.375	0.456	0.300	0.212
Temperature	Min	2.2	3.3	3	1.8	1.1	7.8	4.9	7.8	8.3	2.2	2.5	1.8	2.3	3.4
	Max	14	15	14	18	2	11	5	9	9	17	19	17	11	15
	Mean	7	8	8	9	2	10	5	9	9	12	8	8	7	8
	Median	6	7	7	7	1	10	5	9	9	14	7	6	7	6
	SD	4.680	4.383	4.552	5.984	0.624	1.022	N/A	1.061	0.636	6.925	5.765	5.794	3.142	4.437
	COV	0.655	0.534	0.587	0.691	0.390	0.108	N/A	0.124	0.073	0.584	0.694	0.752	0.432	0.537

		Whisky Stream			Ephemeral channels (Culverts)		Subsurface lateral flow			Upper wetland channel	Lower wetland channel		Control stream	Lake outlet
		WS1	WS2	WS3	RC1	RC2	S1	S4	S5	USW	WC1	WC2	MGS	LS1
pH	25/05/2010 11:30	6.64	6.88	6.96	6.1	NS	NS	NS	NS	NS	6.29	6.38	7.09	6.85
	19/07/2010 12:50	7.9	8.02	7.66	6.54	6.8	NS	NS	NS	NS	6.93	7	7.46	6.8
	9/08/2010 15:15	7.84	7.88	7.6	7.19	6.46	NS	NS	NS	NS	7.2	6.72	7.62	7.11
	1/09/2011 11:15	7.69	7.63	7.64	7.42	NS	NS	NS	NS	NS	7.6	7.55	7.56	7.63
	19/11/2011 14:22	7.1	6.95	6.85	6.31	NS	NS	NS	NS	6.66	6.7	6.51	6.22	6.22
	22/11/2011 11:45	NS	7.9		NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	15/03/2012 12:15	8.13	7.9	7.7	NS	NS	7.6	NS	NS	7.82	7.57	7.8	7.59	8.1
	11/04/2012 12:22	6.68	7.4	6.94	NS	NS	7.04	NS	NS	6.99	6.86	6.8	6.35	6.5
	1/05/2012 14:42	NS	NS	NS	NS	NS	5.93	NS	NS	NS	NS	NS	NS	NS
	11/05/2012 12:20	NS	NS	NS	NS	NS	5.88	6.21	6.44	NS	NS	NS	NS	NS
	14/06/2012 11:25	7.02	7.3	7.26		6.94	7	6.71	6.87	7.4	7.34	7.34	6.94	6.8
DO	25/05/2010 11:30	11.26	12.38	11.02	10.41	NS	NS	NS	NS	NS	10.8	9.79	11.12	11.67
	19/07/2010 12:50	NS	NS	NS	NS	12.8	NS	NS	NS	NS	NS	NS	NS	NS
	9/08/2010 15:15	13.86	13.43	13.06	12.6	13.62	NS	NS	NS	NS	11.66	12.08	12.04	10.82
	1/09/2011 11:15	12	11.9	12.06	10.7	NS	NS	NS	NS	NS	11.63	11.93	11.92	11.44
	19/11/2011 14:22	10.8	9.45	10.6	6.35	NS	NS	NS	NS	9.14	10.66	10.5	11.15	10.4
	22/11/2011 11:45	NS	11.3	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	15/03/2012 12:15	9.75	9.58	9.45	NS	NS	8.95	NS	NS	9.6	10.5	11.5	10.53	9.64
	11/04/2012 12:22	11	10.78	10.9	NS	NS	8.58	NS	NS	10.96	10.75	11.45	10.29	10.52
	1/05/2012 14:42	NS	NS	NS	NS	NS	8.81	NS	NS	NS	NS	NS	NS	NS
	11/05/2012 12:20	NS	NS	NS	NS	NS	9.2	9.9	9	NS	NS	NS	NS	NS
	14/06/2012 11:25	13.39	13.62	13.26		12.29	9	9	10.15	13.4	13.26	12.37	12.29	14

		Whisky Stream			Ephemeral channels (Culverts)		Subsurface lateral flow			Upper wetland channel	Lower wetland channel		Control stream	Lake outlet
		WS1	WS2	WS3	RC1	RC2	S1	S4	S5	USW	WC1	WC2	MGS	LS1
Temperature	**40323.48**	6.8	6.8	6.8	6.9	NS	NS	NS	NS	NS	6.7	6	7.5	7
	19/07/2010 12:50	2.2	4.5	4.3	1.8	1.1	NS	NS	NS	NS	3.7	1.8	5.2	4.8
	9/08/2010 15:15	2.5	3.3	3	6.9	1.4	NS	NS	NS	NS	2.5	2.6	5.1	5.2
	1/09/2011 11:15	5.7	6.3	6.2	9.6	NS	NS	NS	NS	NS	7	6.8	6.3	5.7
	19/11/2011 14:22	13.1	14	14.3	18.1	NS	NS	NS	NS	16.3	18.6	17.2	10.7	14.6
	22/11/2011 11:45	NS	11	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	15/03/2012 12:15	14.2	14.9	14.3	NS	NS	10.5	NS	NS	17.4	14.7	15	9.8	14.3
	11/04/2012 12:22	9.4	9.6	9.6	NS	NS	9.7	NS	NS	11.5	9.9	9.4	11.3	11.1
	1/05/2012 14:42	NS	NS	NS	NS	NS	10	NS	NS	NS	NS	NS	NS	NS
	11/05/2012 12:20	NS	NS	NS	NS	NS	9.5	9.3	9.2	NS	NS	NS	NS	NS
	14/06/2012 11:25	3.3	3.5	3.5	NS	2.3	7.8	7.8	8.3	2.2	3.4	2.8	2.3	3.4
Conductance	**25/05/2010 11:30**	39.5	39.5	39.5	30.7	NS	NS	NS	NS	NS	33.1	31.5	42.1	46.8
	19/07/2010 12:50	30.6	31.8	31.4	36.7	39.5	NS	NS	NS	NS	25	25.8	61.5	62.2
	9/08/2010 15:15	27.5	27.9	27.6	45.3	42.4	NS	NS	NS	NS	26	22.2	36.1	37.2
	1/09/2011 11:15	24.9	25.1	25.1	44.8	NS	NS	NS	NS	NS	26.9	26.7	36.6	35.9
	19/11/2011 14:22	37.5	38.1	38.5	59.6	NS	NS	NS	NS	17.9	30	30.6	39.8	42.1
	22/11/2011 11:45	NS	30.7	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	15/03/2012 12:15	49.3	49.2	47.2	NS	NS	35.6	NS	NS	21.1	45.2	47.6	46.8	43.6
	11/04/2012 12:22	66.8	66.6	66.1	NS	NS	54.6	NS	NS	27.5	64.7	68.7	69	56.6
	1/05/2012 14:42	NS	NS	NS	NS	NS	57.1	NS	NS	NS	NS	NS	NS	NS
	11/05/2012 12:20	NS	NS	NS	NS	NS	56	54.1	63.1	NS	NS	NS	NS	NS
	14/06/2012 11:25	57.5	57.7	56.5	NS	74.3	35.7	33.5	62	12.5	47.1	24.5	74.3	59.5

Appendix E . Sample parameter correlation test results

The following tables are the additional results produced by XLStat for pairwise Pearson correlation analysis of variables for each site. Variables included the month of sampling event; total suspended solids concentration; nutrient concentration and *in-situ* measurement values. Nutrient abbreviations are defined in Section 2.5.4. Dissolved oxygen (DO) and Specific conductivity (SC) are abbreviated.

Summary statistics:

Variable	Observations	Obs. with missing data	Obs. without missing data	Minimum	Maximum	Mean	Std. deviation
Month	153	0	153	3.000	11.000	6.392	2.401
TSS	153	129	24	3.000	200.000	23.500	49.207
TN	153	79	74	0.100	2.200	0.357	0.345
NH4	153	138	15	0.012	0.114	0.030	0.025
NNN	153	97	56	0.002	0.520	0.058	0.108
TKN	153	88	65	0.100	2.200	0.343	0.340
DRP	153	140	13	0.005	0.026	0.011	0.007
P	153	79	74	0.001	0.490	0.025	0.060
pH	153	75	78	5.880	8.130	7.092	0.554
DO	153	83	70	6.350	14.000	11.086	1.512
Temp	153	75	78	1.100	18.600	7.988	4.602
uS	153	75	78	12.500	74.300	42.331	14.853

p-values:

Variables	Month	TSS	TN	NH4	NNN	TKN	DRP	P	pH	DO	Temp	SC
Month	**0**	0.532	0.733	0.797	**0.023**	0.522	0.150	0.450	0.517	0.312	0.940	**0.000**
TSS	0.532	**0**	0.122	**0.029**	**0.026**	0.455	0.609	**0.006**	0.056	0.658	0.628	0.855
TN	0.733	0.122	**0**	0.066	**0.027**	**< 0.0001**	**0.036**	**< 0.0001**	**0.001**	0.532	0.752	0.725
NH4	0.797	**0.029**	0.066	**0**	**0.000**	0.236	0.822	**0.000**	0.058	0.133	0.390	0.323
NNN	**0.023**	**0.026**	**0.027**	**0.000**	**0**	0.130	0.608	**< 0.0001**	**0.001**	**0.008**	0.530	0.335
TKN	0.522	0.455	**< 0.0001**	0.236	0.130	**0**	**0.010**	**< 0.0001**	**0.006**	0.212	0.596	0.378
DRP	0.150	0.609	**0.036**	0.822	0.608	**0.010**	**0**	0.241	0.833	0.310	**0.047**	**0.022**
P	0.450	**0.006**	**< 0.0001**	**0.000**	**< 0.0001**	**< 0.0001**	0.241	**0**	**0.029**	0.163	0.775	0.371
pH	0.517	0.056	**0.001**	0.058	**0.001**	**0.006**	0.833	**0.029**	**0**	0.063	0.504	**0.010**
DO	0.312	0.658	0.532	0.133	**0.008**	0.212	0.310	0.163	0.063	**0**	**< 0.0001**	0.197
Temp	0.940	0.628	0.752	0.390	0.530	0.596	**0.047**	0.775	0.504	**< 0.0001**	**0**	0.403
SC	**0.000**	0.855	0.725	0.323	0.335	0.378	**0.022**	0.371	**0.010**	0.197	0.403	**0**

Values in bold are different from 0 with a significance level alpha=0.05

Coefficients of determination (R^2):

Variables	Month	TSS	TN	NH4	NNN	TKN	DRP	P	pH	DO	Temp	SC
Month	**1**	0.018	0.002	0.005	0.092	0.007	0.179	0.008	0.006	0.015	0.000	0.163
TSS	0.018	**1**	0.105	0.575	0.274	0.028	0.153	0.323	0.170	0.011	0.012	0.002
TN	0.002	0.105	**1**	0.255	0.092	0.952	0.343	0.389	0.149	0.007	0.002	0.002
NH4	0.005	0.575	0.255	**1**	0.879	0.115	0.076	0.696	0.289	0.211	0.068	0.089
NNN	0.092	0.274	0.092	0.879	**1**	0.053	0.025	0.344	0.226	0.161	0.008	0.020
TKN	0.007	0.028	0.952	0.115	0.053	**1**	0.503	0.242	0.127	0.032	0.005	0.014
DRP	0.179	0.153	0.343	0.076	0.025	0.503	**1**	0.122	0.007	0.146	0.453	0.550
P	0.008	0.323	0.389	0.696	0.344	0.242	0.122	**1**	0.071	0.033	0.001	0.012
pH	0.006	0.170	0.149	0.289	0.226	0.127	0.007	0.071	**1**	0.051	0.006	0.084
DO	0.015	0.011	0.007	0.211	0.161	0.032	0.146	0.033	0.051	**1**	0.412	0.025
Temp	0.000	0.012	0.002	0.068	0.008	0.005	0.453	0.001	0.006	0.412	**1**	0.009
SC	0.163	0.002	0.002	0.089	0.020	0.014	0.550	0.012	0.084	0.025	0.009	**1**

Appendix F . PCA results

The following tables are the additional results produced by XLStat for the principal component analysis of variables for each site. Variables included total suspended solids concentration, nutrient concentration and *in-situ* measurement values. Median values used for inputs are shown in the first table below. Site abbreviations are the same as those used in Appendix C. Variable abbreviations are defined in Appendix E.

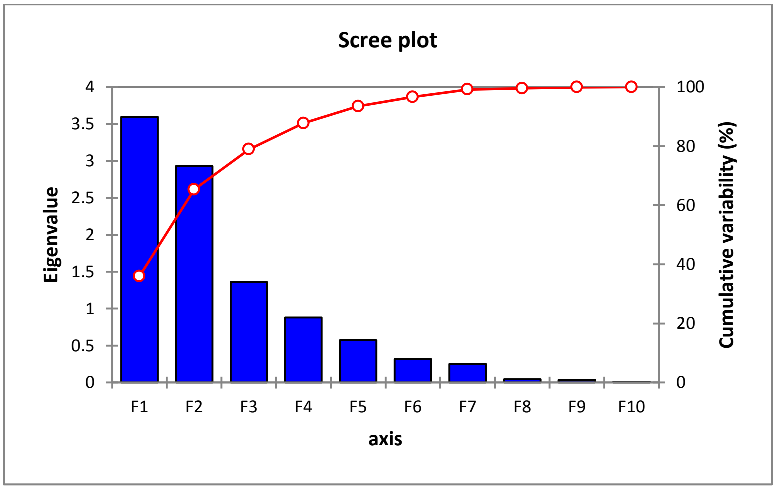
Site	TSS	TN	NH4	NO_3-	TKN	DRP	P	pH	DO	SC
WS1	0.000	0.120	0.012	0.016	0.160	0.010	0.009	7.40	11.26	38.50
WS2	3.000	0.160	0.026	0.005	0.120	0.005	0.008	7.63	11.60	38.10
WS3	6.000	0.160	0.019	0.004	0.160	0.007	0.010	7.430	10.960	39.000
RC1	7.000	0.600	0.063	0.052	0.600	0.013	0.031	6.540	10.700	44.800
RC2	0.000	0.440	0.000	0.004	0.430	0.025	0.019	6.800	12.800	42.400
RC3	55.500	1.280	0.029	0.026	1.250	0.016	0.076	6.670	11.750	43.600
S1	6.000	0.340	0.000	0.270	0.310	0.000	0.016	7.000	8.950	54.600
S4	200.000	0.295	0.000	0.189	0.120	0.000	0.011	6.460	9.450	43.800
S5	0.000	0.315	0.000	0.240	0.000	0.013	0.012	6.655	9.575	62.550
USW	5.500	0.140	0.034	0.008	0.140	0.000	0.029	7.195	10.280	19.500
WC1	4.000	0.220	0.015	0.006	0.220	0.011	0.013	7.065	10.800	31.550
WC2	0.000	0.210	0.028	0.004	0.210	0.007	0.013	6.900	11.500	28.650
WC3	0.000	0.330	0.000	0.010	0.330	0.008	0.014	6.983	11.150	30.100
LS1	4.000	0.565	0.026	0.004	0.565	0.000	0.013	6.825	10.820	45.200
MGS	0.000	0.160	0.000	0.014	0.160	0.005	0.006	7.275	11.150	44.450

Summary statistics:

Variable	Observations	Obs. with missing data	Obs. without missing data	Minimum	Maximum	Mean	Std. deviation
TSS	15	0	15	0.000	200.000	19.400	51.843
TN	15	0	15	0.120	1.280	0.356	0.296
NH4	15	0	15	0.000	0.063	0.017	0.018
NO3-	15	0	15	0.004	0.270	0.057	0.093
TKN	15	0	15	0.000	1.250	0.318	0.308
DRP	15	0	15	0.000	0.025	0.008	0.007
P	15	0	15	0.006	0.076	0.019	0.017
pH	15	0	15	6.460	7.630	6.988	0.345
DO	15	0	15	8.950	12.800	10.850	0.982
SC	15	0	15	19.500	62.550	40.453	10.512

Eigenvalues:

	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10
Eigenvalue	3.599	2.932	1.363	0.881	0.573	0.318	0.250	0.043	0.034	0.008
Variability (%)	35.986	29.317	13.635	8.811	5.729	3.178	2.504	0.425	0.337	0.080
Cumulative %	35.986	65.303	78.938	87.748	93.477	96.655	99.159	99.584	99.920	100.000



Eigenvectors:

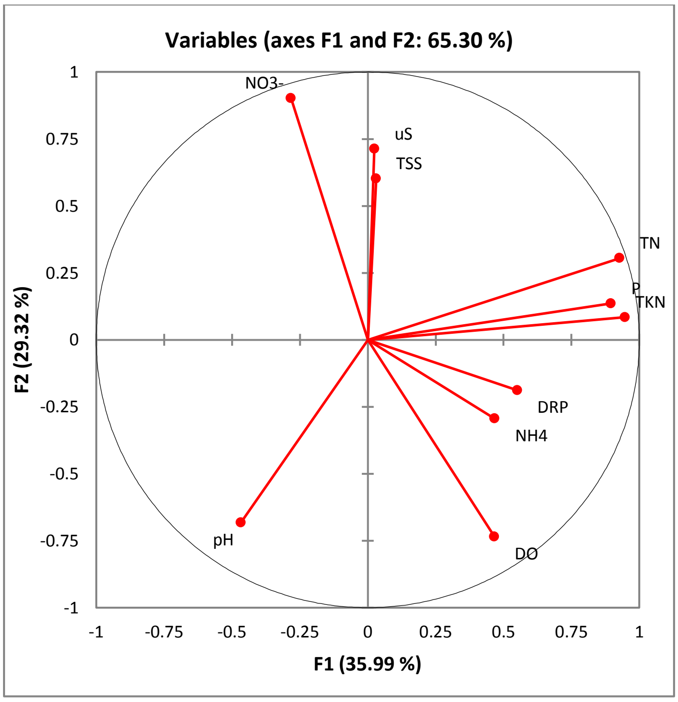
	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10
TSS	0.016	0.351	-0.307	0.697	-0.013	0.372	0.379	-0.077	0.090	-0.010
TN	0.489	0.178	-0.008	-0.053	0.234	0.085	-0.143	-0.042	-0.065	0.799
NH4	0.246	-0.172	-0.465	-0.446	-0.552	0.310	0.272	0.105	0.079	0.042
NO3-	-0.149	0.527	0.105	-0.191	-0.003	-0.252	0.262	0.645	0.308	0.096
TKN	0.499	0.049	-0.067	-0.068	0.302	0.098	-0.252	-0.033	0.633	-0.416
DRP	0.290	-0.110	0.606	0.134	-0.384	-0.209	0.406	-0.291	0.270	0.076
P	0.472	0.079	-0.168	-0.057	0.253	-0.404	0.398	0.025	-0.505	-0.312
pH	-0.247	-0.399	0.002	-0.206	0.577	0.175	0.548	-0.069	0.215	0.151
DO	0.246	-0.429	0.291	0.292	0.016	0.310	-0.041	0.674	-0.172	-0.056
SC	0.013	0.417	0.440	-0.350	0.070	0.593	0.067	-0.139	-0.285	-0.222

Factor loadings:

	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10
TSS	0.031	0.602	-0.359	0.654	-0.010	0.210	0.189	-0.016	0.017	-0.001
TN	0.928	0.305	-0.010	-0.050	0.177	0.048	-0.072	-0.009	-0.012	0.071
NH4	0.467	-0.294	-0.543	-0.419	-0.418	0.175	0.136	0.022	0.015	0.004
NO3-	-0.283	0.902	0.123	-0.179	-0.002	-0.142	0.131	0.133	0.057	0.009
TKN	0.947	0.084	-0.078	-0.063	0.229	0.055	-0.126	-0.007	0.116	-0.037
DRP	0.550	-0.188	0.707	0.126	-0.291	-0.118	0.203	-0.060	0.050	0.007
P	0.896	0.135	-0.197	-0.054	0.191	-0.228	0.199	0.005	-0.093	-0.028
pH	-0.468	-0.683	0.003	-0.194	0.437	0.099	0.274	-0.014	0.039	0.013
DO	0.466	-0.735	0.340	0.274	0.012	0.175	-0.020	0.139	-0.032	-0.005
SC	0.024	0.713	0.513	-0.328	0.053	0.334	0.034	-0.029	-0.052	-0.020

Correlations between variables and factors:

	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10
TSS	0.031	0.602	-0.359	0.654	-0.010	0.210	0.189	-0.016	0.017	-0.001
TN	0.928	0.305	-0.010	-0.050	0.177	0.048	-0.072	-0.009	-0.012	0.071
NH4	0.467	-0.294	-0.543	-0.419	-0.418	0.175	0.136	0.022	0.015	0.004
NO3-	-0.283	0.902	0.123	-0.179	-0.002	-0.142	0.131	0.133	0.057	0.009
TKN	0.947	0.084	-0.078	-0.063	0.229	0.055	-0.126	-0.007	0.116	-0.037
DRP	0.550	-0.188	0.707	0.126	-0.291	-0.118	0.203	-0.060	0.050	0.007
P	0.896	0.135	-0.197	-0.054	0.191	-0.228	0.199	0.005	-0.093	-0.028
pH	-0.468	-0.683	0.003	-0.194	0.437	0.099	0.274	-0.014	0.039	0.013
DO	0.466	-0.735	0.340	0.274	0.012	0.175	-0.020	0.139	-0.032	-0.005
SC	0.024	0.713	0.513	-0.328	0.053	0.334	0.034	-0.029	-0.052	-0.020



Contribution of the variables (%):

	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10
TSS	0.026	12.342	9.445	48.569	0.016	13.854	14.335	0.588	0.815	0.010
TN	23.910	3.170	0.007	0.281	5.472	0.727	2.047	0.175	0.425	63.787
NH4	6.071	2.949	21.655	19.917	30.446	9.629	7.422	1.105	0.627	0.178
NO3-	2.223	27.779	1.113	3.649	0.001	6.344	6.851	41.623	9.499	0.918
TKN	24.915	0.242	0.446	0.456	9.137	0.963	6.337	0.108	40.100	17.294
DRP	8.412	1.208	36.706	1.801	14.734	4.363	16.443	8.455	7.294	0.584
P	22.301	0.625	2.837	0.330	6.385	16.317	15.877	0.061	25.544	9.724
pH	6.081	15.897	0.001	4.252	33.287	3.058	30.074	0.477	4.601	2.271
DO	6.045	18.438	8.471	8.515	0.024	9.590	0.166	45.480	2.958	0.314
SC	0.017	17.349	19.318	12.229	0.497	35.155	0.449	1.929	8.137	4.920

Squared cosines of the variables:

	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10
TSS	0.001	0.362	0.129	**0.428**	0.000	0.044	0.036	0.000	0.000	0.000
TN	**0.860**	0.093	0.000	0.002	0.031	0.002	0.005	0.000	0.000	0.005
NH4	0.218	0.086	**0.295**	0.175	0.174	0.031	0.019	0.000	0.000	0.000
NO3-	0.080	**0.814**	0.015	0.032	0.000	0.020	0.017	0.018	0.003	0.000
TKN	**0.897**	0.007	0.006	0.004	0.052	0.003	0.016	0.000	0.013	0.001
DRP	0.303	0.035	**0.500**	0.016	0.084	0.014	0.041	0.004	0.002	0.000
P	**0.803**	0.018	0.039	0.003	0.037	0.052	0.040	0.000	0.009	0.001
pH	0.219	**0.466**	0.000	0.037	0.191	0.010	0.075	0.000	0.002	0.000
DO	0.218	**0.541**	0.116	0.075	0.000	0.030	0.000	0.019	0.001	0.000
SC	0.001	**0.509**	0.263	0.108	0.003	0.112	0.001	0.001	0.003	0.000

Values in bold show the variable and corresponding factor for which the squared cosine is the largest

Factor scores:

Observation	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10
WS1	-1.055	-1.335	0.562	0.032	0.238	0.168	0.443	-0.109	0.135	-0.083
WS2	-1.167	-1.870	-0.184	-0.383	0.466	0.857	0.714	0.306	0.005	0.164
WS3	-1.070	-1.236	-0.025	-0.240	0.293	0.400	0.462	-0.261	0.042	0.002
RC1	2.409	0.387	-0.768	-1.317	-1.824	0.427	0.148	-0.074	0.161	-0.063
RC2	1.564	-1.062	2.681	1.214	-0.526	-0.115	-0.047	0.193	0.069	-0.069
RC3	5.782	0.937	-0.299	0.202	1.242	-0.157	0.391	-0.019	-0.099	0.021
S1	-1.534	2.848	0.121	-1.434	1.003	-0.477	-0.076	0.241	0.331	-0.075
S4	-1.358	3.630	-1.388	2.365	-0.350	0.485	0.239	0.000	0.026	-0.005
S5	-1.176	2.790	1.933	-0.975	-0.660	-0.366	0.210	-0.085	-0.354	0.112
USW	-0.725	-1.390	-2.286	-0.227	-0.087	-1.084	0.275	0.022	-0.250	-0.058
WC1	-0.452	-0.999	0.036	0.308	-0.339	-0.529	-0.022	-0.387	0.214	0.076
WC2	-0.180	-1.343	-0.544	0.278	-0.818	-0.241	-0.410	0.426	-0.074	-0.007
WC3	-0.250	-0.835	0.202	0.727	0.377	-0.713	-0.739	-0.055	0.135	0.119
LS1	0.595	0.175	-0.726	-0.633	0.266	0.898	-1.294	-0.076	-0.072	0.048
MGS	-1.385	-0.696	0.684	0.082	0.721	0.446	-0.293	-0.122	-0.268	-0.180

Contribution of the observations (%):

	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10
WS1	2.061	4.052	1.547	0.008	0.658	0.595	5.236	1.874	3.598	5.748
WS2	2.522	7.948	0.165	1.110	2.522	15.421	13.561	14.686	0.004	22.496
WS3	2.123	3.474	0.003	0.437	0.997	3.353	5.687	10.689	0.344	0.005
RC1	10.755	0.340	2.885	13.116	38.697	3.827	0.583	0.863	5.138	3.356
RC2	4.534	2.565	35.144	11.159	3.222	0.279	0.059	5.837	0.946	4.034
RC3	61.933	1.996	0.436	0.308	17.950	0.518	4.075	0.057	1.924	0.359
S1	4.358	18.448	0.072	15.559	11.712	4.769	0.152	9.138	21.704	4.752
S4	3.417	29.957	9.417	42.335	1.428	4.931	1.519	0.000	0.133	0.021
S5	2.560	17.697	18.267	7.194	5.076	2.808	1.173	1.123	24.861	10.560
USW	0.973	4.393	25.549	0.388	0.089	24.674	2.008	0.073	12.383	2.829
WC1	0.379	2.270	0.006	0.716	1.335	5.868	0.013	23.506	9.033	4.789
WC2	0.060	4.102	1.446	0.586	7.792	1.215	4.480	28.447	1.094	0.045
WC3	0.116	1.586	0.199	4.003	1.650	10.651	14.561	0.471	3.607	11.861
LS1	0.656	0.069	2.577	3.031	0.826	16.909	44.603	0.903	1.020	1.904
MGS	3.553	1.102	2.288	0.050	6.045	4.182	2.290	2.335	14.209	27.239

Squared cosines of the observations:

	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10
WS1	0.315	**0.505**	0.090	0.000	0.016	0.008	0.056	0.003	0.005	0.002
WS2	0.206	**0.528**	0.005	0.022	0.033	0.111	0.077	0.014	0.000	0.004
WS3	0.351	**0.469**	0.000	0.018	0.026	0.049	0.065	0.021	0.001	0.000
RC1	**0.490**	0.013	0.050	0.146	0.281	0.015	0.002	0.000	0.002	0.000
RC2	0.195	0.090	**0.571**	0.117	0.022	0.001	0.000	0.003	0.000	0.000
RC3	**0.924**	0.024	0.002	0.001	0.043	0.001	0.004	0.000	0.000	0.000
S1	0.169	**0.582**	0.001	0.147	0.072	0.016	0.000	0.004	0.008	0.000
S4	0.080	**0.574**	0.084	0.244	0.005	0.010	0.002	0.000	0.000	0.000
S5	0.095	**0.533**	0.256	0.065	0.030	0.009	0.003	0.000	0.009	0.001
USW	0.058	0.213	**0.577**	0.006	0.001	0.130	0.008	0.000	0.007	0.000
WC1	0.108	**0.527**	0.001	0.050	0.061	0.148	0.000	0.079	0.024	0.003
WC2	0.010	**0.548**	0.090	0.024	0.203	0.018	0.051	0.055	0.002	0.000
WC3	0.024	**0.272**	0.016	0.207	0.055	0.198	0.213	0.001	0.007	0.006
LS1	0.091	0.008	0.136	0.103	0.018	0.208	**0.432**	0.001	0.001	0.001
MGS	**0.505**	0.127	0.123	0.002	0.137	0.052	0.023	0.004	0.019	0.009

Values in bold show the variable and corresponding factor for which the squared cosine is the largest

Appendix G . Non-parametric Dwass-Steel-Critchlow-Fligner method

The following tables are the additional results produced by XLStat for a non-parametric one-way analysis of variance (Dwass-Steel-Critchlow-Fligner method) for total nitrogen (TN) and total phosphorus (TP) at each site. Site abbreviations are the same as those used in Appendix C.

Kruskal-Wallis test (TN):

K (Observed value)	52.903
K (Critical value)	23.685
DF	14
p-value (Two-tailed)	< 0.0001
alpha	0.05

An approximation has been used to compute the p-value.

Test interpretation:
H0: The samples come from the same population.
Ha: The samples do not come from the same population.
As the computed p-value is lower than the significance level alpha=0.05, one should reject the null hypothesis H0, and accept the alternative hypothesis Ha.
The risk to reject the null hypothesis H0 while it is true is lower than 0.01%.

Ties have been detected in the data and the appropriate corrections have been applied.

Multiple pairwise comparisons using the Steel-Dwass-Critchlow-Fligner procedure / Two-tailed test:

Sample	Frequency	Sum of ranks	Mean of ranks	Groups
TN | MGS	3	50.500	16.833	A
TN | WS1	7	130.500	18.643	A
TN | WS3	8	154.000	19.250	A
TN | WS2	10	195.000	19.500	A
TN | USW	3	58.500	19.500	A
TN | WC1	7	241.500	34.500	A
TN | WC2	5	178.000	35.600	A
TN | S4	2	84.000	42.000	A
TN | S5	2	90.500	45.250	A
TN | WC3	3	138.000	46.000	A
TN | S1	5	263.000	52.600	A
TN | RC2	3	177.000	59.000	A
TN | RC3	3	186.000	62.000	A
TN | LS1	8	497.500	62.188	A
TN | RC1	5	331.000	66.200	A

Wij (non-negative weights):

	TN | WS1	TN | WS2	TN | WS3	TN | RC1	TN | RC2	TN | RC3	TN | S1	TN | S4	TN | S5	TN | USW	TN | WC1	TN | WC2	TN | WC3	TN | LS1	TN | MGS
TN | WS1		-0.347	0.000	-4.033	-3.405	-3.405	-4.040	-2.923	-2.923	-0.491	-2.271	-2.078	-2.602	-4.595	-0.164
TN | WS2	0.347		0.063	-4.334	-3.591	-3.591	-4.338	-3.044	-3.044	0.120	-2.351	-2.697	-2.996	-5.031	0.361
TN | WS3	0.000	-0.063		-4.146	-3.472	-3.335	-4.152	-2.786	-2.963	-0.145	-2.297	-2.387	-2.893	-4.760	0.435
TN | RC1	4.033	4.334	4.146		2.545	-0.632	2.815	2.739	2.739	3.162	4.019	3.693	2.741	1.142	3.162
TN | RC2	3.405	3.591	3.472	-2.545		-0.926	1.909	2.449	2.449	2.777	3.384	2.741	1.543	-1.305	2.777
TN | RC3	3.405	3.591	3.335	0.632	0.926		1.060	1.257	0.816	2.777	2.417	2.319	1.543	1.157	2.777
TN | S1	4.040	4.338	4.152	-2.815	-1.909	-1.060		2.211	1.658	3.181	1.956	2.222	1.060	-2.283	3.181
TN | S4	2.923	3.044	2.786	-2.739	-2.449	-1.257	-2.211		-1.732	2.449	0.414	0.829	-0.816	-2.963	2.449
TN | S5	2.923	3.044	2.963	-2.739	-2.449	-0.816	-1.658	1.732		2.449	0.624	1.382	-0.816	-2.963	2.449
TN | USW	0.491	-0.120	0.145	-3.162	-2.777	-2.777	-3.181	-2.449	-2.449		-1.784	-1.897	-2.160	-3.472	0.000
TN | WC1	2.271	2.351	2.297	-4.019	-3.384	-2.417	-1.956	-0.414	-0.624	1.784		-0.230	-1.450	-3.931	1.940
TN | WC2	2.078	2.697	2.387	-3.693	-2.741	-2.319	-2.222	-0.829	-1.382	1.897	0.230		-1.697	-3.731	2.969
TN | WC3	2.602	2.996	2.893	-2.741	-1.543	-1.543	-1.060	0.816	0.816	2.160	1.450	1.697		-2.755	2.777
TN | LS1	4.595	5.031	4.760	-1.142	1.305	-1.157	2.283	2.963	2.963	3.472	3.931	3.731	2.755		3.472
TN | MGS	0.164	-0.361	-0.435	-3.162	-2.777	-2.777	-3.181	-2.449	-2.449	0.000	-1.940	-2.969	-2.777	-3.472	

Kruskal-Wallis test (TP):

K (Observed value)	34.786
K (Critical value)	23.685
DF	14
p-value (Two-tailed)	0.002
alpha	0.05

An approximation has been used to compute the p-value.

Test interpretation:
H0: The samples come from the same population.
Ha: The samples do not come from the same population.
As the computed p-value is lower than the significance level alpha=0.05, one should reject the null hypothesis H0, and accept the alternative hypothesis Ha.
The risk to reject the null hypothesis H0 while it is true is lower than 0.16%.

Ties have been detected in the data and the appropriate corrections have been applied.

Multiple pairwise comparisons using the Steel-Dwass-Critchlow-Fligner procedure / Two-tailed test:

Sample	Frequency	Sum of ranks	Mean of ranks	Groups
TP | MGS	7	109.000	15.571	A
TP | WS1	7	153.000	21.857	A
TP | WS2	7	160.000	22.857	A
TP | S4	2	58.000	29.000	A
TP | WS3	7	223.000	31.857	A
TP | S5	2	70.500	35.250	A
TP | WC2	8	288.500	36.063	A
TP | LS1	8	332.500	41.563	A
TP | WC1	7	293.500	41.929	A
TP | WC3	3	127.500	42.500	A
TP | USW	2	101.500	50.750	A
TP | S1	3	157.500	52.500	A
TP | RC2	3	178.000	59.333	A
TP | RC3	3	185.000	61.667	A
TP | RC1	5	337.500	67.500	A

Wij (non-negative weights):

	P | WS1	P | WS2	P | WS3	P | RC1	P | RC2	P | RC3	P | S1	P | S4	P | S5	P | USW	P | WC1	P | WC2	P | WC3	P | LS1	P | MGS
P | WS1		-0.273	-1.367	-3.566	-2.748	-3.071	-2.425	-0.209	-1.879	-2.495	-2.357	-2.468	-2.425	-2.787	0.731
P | WS2	0.273		-1.181	-4.026	-2.748	-3.071	-2.748	0.209	-1.663	-2.296	-2.365	-2.473	-2.270	-2.800	1.364
P | WS3	1.367	1.181		-3.451	-2.095	-2.740	-1.617	0.624	-0.624	-1.871	-1.272	-0.986	-1.293	-1.394	2.097
P | RC1	3.566	4.026	3.451		1.897	-0.211	2.969	2.739	2.739	1.095	3.227	4.152	3.162	4.146	4.033
P | RC2	2.748	2.748	2.095	-1.897		-0.926	1.543	2.449	2.449	0.000	1.455	3.480	2.777	2.325	3.405
P | RC3	3.071	3.071	2.740	0.211	0.926		0.926	1.633	1.633	1.633	2.270	2.336	1.543	2.315	3.253
P | S1	2.425	2.748	1.617	-2.969	-1.543	-0.926		1.257	2.094	0.000	0.973	2.781	1.589	1.595	3.405
P | S4	0.209	-0.209	-0.624	-2.739	-2.449	-1.633	-1.257		0.000	-1.095	-0.832	-0.186	-0.419	-1.111	1.269
P | S5	1.879	1.663	0.624	-2.739	-2.449	-1.633	-2.094	0.000		-1.095	-0.832	0.000	-1.257	-0.929	2.115
P | USW	2.495	2.296	1.871	-1.095	0.000	-1.633	0.000	1.095	1.095		0.842	0.932	0.419	0.557	2.505
P | WC1	2.357	2.365	1.272	-3.227	-1.455	-2.270	-0.973	0.832	0.832	-0.842		0.825	0.163	0.411	2.998
P | WC2	2.468	2.473	0.986	-4.152	-3.480	-2.336	-2.781	0.186	0.000	-0.932	-0.825		-1.174	-1.046	3.294
P | WC3	2.425	2.270	1.293	-3.162	-2.777	-1.543	-1.589	0.419	1.257	-0.419	-0.163	1.174		-0.291	3.081
P | LS1	2.787	2.800	1.394	-4.146	-2.325	-2.315	-1.595	1.111	0.929	-0.557	-0.411	1.046	0.291		3.610
P | MGS	-0.731	-1.364	-2.097	-4.033	-3.405	-3.253	-3.405	-1.269	-2.115	-2.505	-2.998	-3.294	-3.081	-3.610	